Cleaning Technology in Semiconductor Device Manufacturing VIII

Proceedings of the International Symposium

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PREFACE

The Eighth International Symposium on Cleaning Technology in Semiconductor Device Manufacturing was held during the Fall Meeting of the Electrochemical Society in Orlando, Florida in October 2003. This series of symposia was initiated in 1989 during the Society Fall Meeting in Hollywood, Florida. Since then, the "ECS Cleaning Symposium" has become a bi-annual event of interest to the members of the semiconductor community involved with advanced wafer cleaning and surface conditioning technology. Reaching back, we can identify several important new developments in silicon wafer cleaning science and engineering that were first considered during the ECS Cleaning Symposia.

For fourteen years now, the ECS Cleaning Symposia have been reflecting progress in wafer cleaning technology. During those years this critically important operation in any semiconductor device manufacturing process underwent significant quantitative and qualitative changes. The content of this volume reflects these changes with a few trends being immediately apparent. For instance, distinction between FEOL and BEOL cleans has become very clear with the latter attracting systematically growing attention of cleaning engineers and scientists. Also, single-wafer cleaning is getting close to becoming a mainstream technology. Ozonated water, high-k gate dielectrics, low-k inter-layer dielectrics, copper interconnects, post-CMP cleans, MEMS cleaning, supercritical and cryogenic cleaning are the concepts discussed in detail throughout this volume. However, none of them had been present yet in the discussion during the first ECS Cleaning Symposium in 1989.

We would like to take this opportunity to thank all symposium authors and participants who turned this into a very informative and productive meeting. In particular, we would like to thank those among the authors who were involved in the preparation of the final camera-ready version of the respective manuscripts. Our thanks are also due to the invited speakers for their excellent contributions and to all the participants for their encouragement and support. We are looking forward to the ninth symposium in this series to be held during the ECS Fall 2005 meeting in Los Angeles.

> Jerzy Ruzyllo Takeshi Hattori Robert L. Opila Richard E. Novak

iii

TABLE OF CONTENTS

Preface	iii
THE SCIENCE AND TECHNOLOGY OF THE FUNCTIONAL WATER M. Toda and S. Uryuu (Invited)	1
Single Wafer Cleaning	13
EFFECTIVE POST-ETCH RESIDUE REMOVAL ON LOW-K FILMS USING SINGLE WAFER PROCESSING	
E. Kesters , J. Ghekiere, P. Van Doorne, G. Vereecke, P.W. Mertens, and M.M. Heyns	15
AQUEOUS SINGLE PASS SINGLE WAFER AI/VIA CLEANING S. Verhaverbeke, C. Beaudry, and P. Boelen	23
IMPROVED RINSING EFFICIENCY ON POST-ETCH RESIDUE WET CLEAN FOR Cu/LOW-k DAMASCENE STRUCTURES C.K. Chang, C.F. Tsang V. Nguyen, Q. Zhang, and T.H. Foo	27
SINGLE WAFER WET CLEANING BASED ON SHORT CYCLE TIME, AMBIENT TEMPERATURE AND A SMALL AMOUNT OF CHEMICAL	
KI. Sano and A. Izumi	34
INNOVATIVE SURFACE PREPARATION SOLUTIONS FOR SUB- 90 nm IC DEVICES	10
E. Baiya, J. Rosato, and R. Yalamanchili	42
PREDICTIVE MODEL-BASED CONTROL OF CRITICAL OXIDE ETCHES FOR SUB-100 nm PROCESSES IN A SINGLE WAFER WET PROCESSING SYSTEM	
Y. Lu, M.R. Yalamanchili, and J. Rosato	49
NON-IPA WAFER DRYING TECHNOLOGY FOR SINGLE-SPIN WET CLEANING	
K. Miya, T. Kishimoto, and A. Izumi	57

v

Front End of the Line Cleaning

INTEGRATION OF HIGH-K GATE DIELECTRICS – WET ETCH	
S. De Gendt, S. Beckx, M. Caymax, M. Claes, T. Conard, A. Delabie,	
W. Deweerd , D. Hellin, H. Kraus, B. Onsia, V. Parishev, R. Puurunen, E. Rohr,	
J. Snow, W. Tsai, P. Van Doorne, S. Van Elshocht, J. Vertommen,	(7
T. Witters, and M. Heyns (Invited)	67
STUDY OF THE EFFECT OF SILICON SURFCE TREATMENT	
ON EOT IN HIGH-k DIELECTRIC MOS GATE STACK	
K. Chang, K. Shanmugasundaram, DO. Lee, P. Roman J. Shallenberger,	
FM. Chang, J. Wang, R. Beck P. Mumbauer, R. Grant, and J. Ruzyllo	78
ATOMIC LAYER DEPOSITION OF SILICON NITRIDE BARRIER	
LAYER FOR SELF-ALIGNED GATE STACK	
C. Finstad and A. Muscat	86
GUD MANOMETER HIGH IZ CATE OTACIZ COAT DIC HODIC THE	
SUB-NANOMETER HIGH -K GATE STACK SCALING USING THE	
J. Peterson, J. Barnett, C. Young, A. Hou, J. Gutt, S. Gonalan, C.H. Lee	
H.J. Li, N. Moumen, N. Chaudhary, B.H. Lee, G. Bersuker, P. Zietzoff,	
G.A. Brown, P. Lysaght, M. Gardner, R.W. Murto, and H. Huff	93
IMPROVEMENTS IN ADVANCED GATE OVIDE ELECTRICAL	
PERFORMANCE BY THE USE OF AN OZONATED WATER	
CLEAN RPOCESS	
J. Barnett, N. Moumen, and D. Riley	100
EFFECT OF DIE SEQUENCE AND DOST DIE SUBEACE	
PROCESSING ON THE RELIABILITY OF GATE OXIDE IN	
A TRENCH	
T. Grebs, R. Ridley, K.Chang, CT. Wu, R. Agarwal, J. Mytych,	
W. Dimachkie, G. Dolny, J. Michalowicz, and J. Ruzyllo	108
MINIMIZING OXIDE LOSS IN IMMERSION SC.1 PROCESS	
J. Butterbaugh, S. Loper, and T. Wagener	116
PERFORMANCE OF AN ADVANCED FRONT OF THE LINE	
CLEAN COMPARED TO THE PROCESS OF RECORD CLEAN	
IN A MANUFACIUKING ENVIKUNMENI R Novak I Kashkoush I Nolan I Hunter and I Straight	123
is moras, i masimousii, s. moraily s. multer, and s. suraight	120

vi

THE MECHANISM OF POLY-Si ETCHING DURING POLY/W GATE CLEANING BY FLUORINE BASED CLEANING SOLUTION	
S.Y. Kim, S.J. Choi, C.K. Hong, W.S. Han, and J.T. Moon	129
Physical and Chemical Methods of Particle Removal	135
MECHANISMS OF PARTICLE REMOVAL DURING BRUSH SCRUBBER CLEANING K. Xu, R. Vos, G. Vereecke, P. Mertens, M. Heyns, C. Vinckier, and J. Fransaer	137
EVALUATION OF MEGASONIC CLEANING SYSTEMS FOR PARTICLE REMOVAL EFFICIENCY AND DAMAGING G. Vereecke, F. Holsteyns , J. Veltens, M. Lux, S. Arnauts, K. Kenis, R. Vos, P. Mertens, and M. Heyns	145
MECHANICAL RESISTANCE OF FINE MICROSTRUCTURES RELATED TO PARTICLE CLEANING MECHANISMS F. Tardif, O. Raccurt, J.C. Barbe, F. De Crecy, P. Besson, and A. Danel	153
EVALUATION OF MEGASONIC CLEANING PROCESSES F. Holsteyns, A. Riskin, A. Maes, G. Vereecke, and P.W. Mertens	161
STUDY OF THE CLEANING CONTROL USING A MEGAHERTZ NOZZLE SOUND PRESSURE MONITOR SYSTEM FOR SINGLE-PLATE SPIN CLEANERS H. Fujita, N. Hayamizu, T. Goshizono, and N. Sakurai	168
EXPERIMENTAL VALIDATION OF A SCIENCE-BASED UNDERCUT REMOVAL MODEL FOR THE CLEANING OF MICRON-SCALE PARTICLES FROM SURFACES G. Kumar. and S. Beaudoin	176
RESONANCE DAMAGE OF SEMICONDUCTORS BY ACOUSTIC EXCITATION	1,0
K. Christenson SUBSTRATE DAMAGE-FREE LASER SHOCK CLEANING	182
OF PARTICLES J.G. Park , A. Busnaina, J.M. Lee, and S.Y. You	190

EFFECT OF SURFACTANTS ON PARTICLE CONTAMINATION OF SILICON SURFACE IN HF SOLUTIONS T. Vehmas, H. Ritala, and O. Anttila	195
Supercritical, Cryogenic, and Dry Cleaning	203
IN SITU PROCESS FOR PERIODIC CLEANING OF LOW	
TEMPERATURE NITRIDE FURNACES D. Foster, R. Herring, J. Ellenberg, A. Johnson, and C. Hartz	205
MAKING SUPERCRITICAL CO2 CLEANING WORK: PROPER SELECTION OF CO-SOLVENTS AND OTHER ISSUES	
A. Sehgal	214
CHEMICAL ADDITIVE FORMULATIONS FOR SILICON SURFACE CLEANING IN SUPERCRITICAL CARBON DIOXIDE	
M. Korzenski, C. Xu, T. Baum, K. Saga, H. Kuniyasu, and T. Hattori	222
SURFACTANT ENABLED SUPERCRITICAL CO ₂ CLEANING PROCESSES FOR BEOL APPLICATIONS: POST-BARRIER BREAKTHROUGH	
J. DeYoung, S. Gross, M. Wagner, Z. Hatcher, and C. Ma	232
CO ₂ – EXPANDED LIQUIDS AS ALTERNATIVES TO CONVENTIONAL SOLVENTS FOR RESIST AND RESIDUE	
M. Spuller and D. Hess	240
PHOTORESIST STRIPPING USING SUPERCRITICAL CO ₂ – BASED PROCESSES	
V. Perrut, A. Danel, C. Millet, J. Daviot, M. Rignon, and F. Tardif	246
POST-ETCH CLEANING OF 300 mm DUAL DAMASCENE LOW-k DIELECTRIC STRUCTURES USING SUPERCRITICAL CO ₂ R.B. Turkot, Jr., V.S. RamachandraRao, S.A. Iyer, and S.C. Clark	254
IMPACT OF PHASE BEHAVIOR ON PHOTRESIST REMOVAL	
G. Levitin, S. Myneni, and D. Hess	263
COPPER LOW-k CONTAMINANTION AND POST ETCH RESIDUES REMOVAL USING SUPERCRITICAL CO2-BASED	
C. Millet, J. Daviot, A. Danel, V. Perrut, F. Tardif, L. Broussous, and O. Renault	271

WATER REMOVAL AND REPAIR OF POROUS ULTRA-LOW k FILMS USING SUPERCRITICAL CO ₂ B. Xie and A. Muscat	279
CLEANING OF FRAGILE FINE STRUCTURERS WITH CRYOGENIC NITROGEN AEROSOLS H. Saito, A. Munakata, D. Ichishima, T. Yamanishi, A. Okamoto, K. Saga, H. Kuniyasu, and T. Hattori	289
Post-CMP Cleaning	297
ADVANCED FRONT END OF THE LINE CLEAN FOR POST-CMP PROCESSES I. Kashkoush, T. Nolan, D. Nemeth, and R. Novak	299
LOW CARBON CONTAMINATION AND WATER MARK FREE POST-CMP CLEANING OF HYDROPHOBIC OSG DIELECTRICS K. Bartosh, E. Brown, S. Naghshineh, D. Peters, and E. Walker	305
ADHESION AND REMOVAL OF SILICA AND ALUMINA SLURRY PARTICLES DURING Cu CMP PROCESS J. Park and A.A. Busnaina	312
POST-COPPER CMP CLEANING GALVANIC PHENOMENON INVESTIGATED BY EIS C. Gabrielli, E. Ostermann, H. Perrot, and S. Mege	321
AQUEOUS CRYOGENICALLY ENHANCED POST-COPPER CMP	
S. Banerjee, A. Via, S. Joshi, and J. Eklund	329
Organic and Metal Contaminant Removal	338
CHARACTERIZING ETCH RESIDUE REMOVAL FROM LOW-k ILD STRUCTURES USING AQUEOUS AND NON-AQUEOUS CHEMISTRIES	
J. Moore and C. Meuchel	340
REVERSING OF SILICON SURFACE AGING BY LAMP CLEANING K. Shanmugasundaram, K. Chang, J. Shallenberger, A. Danel, F. Tardif, and J. Ruzyllo	348

SUBJECT INDEX	432
AUTHOR INDEX	428
OPEN CIRCUIT AND GALVANOSTATIC BEHAVIOR OF COPPER OXIDIZED AND REDUCED IN VARIOUS SOLUTIONS M. Hughes, S. Naghshineh, and D. Peters	421
INFLUENCE OF ALUMINUM BOND PAD SURAFACE CONDITION ON PROBE ABILITY K. Gunturu, C. Hatcher, K. Burnside, T. Corsetti, R. Lappan, and J. Prasad	414
BEHAVIOUR OF ALUMINUM IN OZONATED WATER, OPTICAL AND ELECTROCHEMICAL STUDY H. Ritala, A. Pehkonen, K. Solehmainen, and L. Grönberg	406
PASSIVATION OF ALUMINUM AND ALUMINUM COPPER ALLOYS IN AQUEOUS ACID I. Rink and M. Knotter	400
CLEANING OF METAL GATE STACKS FOR THE SUB 90 nm TECHNOLOGY NODE J. Snow, H. Kraus, K. Vermeyen, W. Fyen, P. Mertens, and F. Kovacs	393
CLEANING CHEMISTRY WITH COMPLEXING AGENTS (CAs): DECOMPOSITION OF CAs IN HYDROGEN PEROXIDE AND APM STUDIED WITH HPLC S. Metzger and B.O. Kolbesen	386
DEGRADATION OF OXIDE PROPERTIES CAUSED BY LOW-LEVEL METALLIC CONTAMINATION A. Hoff, E. Oborina, S. Aravamudhan, and A. Isti	379
ADDITIVE TECHNOLOGIES FOR SUB 100 nm DEVICE CLEANING H. Morinaga, A. Itou, H. Mochizuki, and M. Ikemoto	371
CLEANING CHEMISTRY WITH COMPLEXING AGENTS (CAs): CA DEGRADATION MONITORING BY UV/VIS SPECTROSCOPY O. Doll and B. Kolbesen	362
ADVANCED PHOTO RESIST REMOVAL USING O ₃ AND MOIST UPW IN SEMICONDUCTOR PRODUCTION G. Philit, L. von Aswege, M. Madore, K. Wolke, MC. Clech, E. Asselin-Degrange, A. Chabli, and D. Louis	356

x



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THE SCIENCE AND TECHNOLOGY OF THE FUNCTIONAL WATER

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ABSTRACT

The water, which is the base of functional water, is simply described. Then, the definition of the functional water will be explained clearly. At first of all, it is simply touched on the RCA cleaning solution. Afterwards, from the viewpoint of radical activation of cleaning solution, the characteristics of the functional water such as the ultrasonic wave excitation water, the ultraviolet irradiation water, ozonized water, active species that are created in hydrogen peroxide water and in the dilute hydrofluoric acid solution will be mentioned briefly.

INTRODUCTION

The water is closely related to the human race since historic times and a source of all lives on the earth too. Therefore, the people pay the special attention for water and the expectation is also made to water. It was not exaggeration to say that the delicate and advanced cleaning technology of surface began from the cleaning of wafer surface in semiconductor manufacturing. RCA cleaning method proposed by Werner Kern et al. [1] in 1970 is used in the silicon wafer surface cleaning throughout more over quarter of century. From the problems of waste water treatment, reusing of resources and environmental pollution, the new cleaning solutions called as functional water based on ultra pure water and using a little amount of chemicals instead of RCA cleaning solutions is recently noticed.

In this study, the water, which is the base of functional water, is simply described. Then, the definition of functional water will be explained clearly. At first of all, it is simply touched on the RCA cleaning solution. Afterwards, from the viewpoint of radical activation of cleaning solutions, the characteristics of functional water such as the ultrasonic wave excitation water, the ultraviolet irradiation water, ozonized water, active species that are created in hydrogen peroxide water and in the dilute hydrofluoric acid solution, etc. will be mentioned briefly.

STRUCTURE OF WATER AND AVERAGE VACANCY VOIDAGE



Figure 1 Structure of ice and water by computer simulation (The Americation for the Advancement of Molecular Science : "Shin - Bunshinorekat", Kenakutolin Inc. (1995) It is clear that the base of the function water is water itself. Therefore, it is very important to rightly understand the structure and the property of water for an accurate understanding of the function water. Figure 1 shows the structure of water calculated by computer simulation [2]. The structure of ice is illustrated in the left-hand side of Figure 1, and the structure of water is also shown in

the right-hand side of Figure 1. In the figure, small sphere means the hydrogen atom, and large sphere means the oxygen atom, respectively. The size of the average hole has been estimated at about 5\AA in the structure of the water. And the water molecule without hydrogen bond vibrates at about 1000 GHz. It can be said that the water is very interesting materials having many void. It tries to obtain the average void in the water from the simple estimation as a whole.

Figure 2 shows the estimation method of average void of water. In this estimation, the shape of water is assumed to be sphere and its diameter is also assumed to be 2.98×10^{-1} nm. The molecular weight of the water is 18 [g/mol] and the density of water is 0.99704 [g/cm³] at 25°C. Therefore, the molecular numbers in 1 cm³ can be explained by the equation as shown in Figure 2. In the calculation, 6.0221367×10^{23} [1/mol] was



Figure 2 Void in ultra pure water of 1 cm³

used as a value of Avogadro number. When the void in 1cm^3 of water is made to be ε , its value becomes 0.5378 as shown in Figure 2. It is noted that there is so many vacancy in water. This is the one of special feature of water. As the other characteristics, the followings are mentioned: (1) the boiling point of water is higher than other hydride, (2) water have large dielectric constant, (3) the water molecule has the polarity, etc.

DEFFINITION OF FUNCTIONAL WATER

According to S. Kubota et al. [3], the water of which the activity is higher than usual water is called as the active water. Especially, as the tap water is purified by various methods and the dissolved gas is controlled, the water treated by physical-chemical processing such as electrolysis, chemicals addition, light irradiation, ultrasonic excitation and magnetism, etc. in order to give the special function is called as the functional water. Afterwards, Kubota defined all water artificially processed in having some purposes as the functional water. In the functional water, the following phenomenon occurs when the water is treated by the physical and chemical method; 1. Clustery size and structure of water change, 2. The radical that is very active chemical species is formed, 3. The active species is formed by the reaction between radical and dissolved gas, 4. Oxidation-reduction potential change. Ultimately, the physical properties such as dielectric constant, viscous force, electric conductivity, surface tension, and oxidation-reduction potential tend to change. Therefore, it is very important to clearly understand the various phenomena such as physical property change and generation of active chemical species due to irradiation of ultrasonic wave to ultra pure water and dilute chemical solution used in wafer cleaning process and so on.

RADICAL ACTIVATION IN EACH FUNCTIONA WATERS

In this work, either function water is also examined experimentally from the viewpoint of the radical generation in the solutions. OH radical is one of the active oxygen, and OH radical has a very strong oxidation power.

RCA Cleaning Solution

Figure 3 indicates RCA cleaning solutions and its mixing ratio. Werner Kern et al. of RCA Co., Ltd., proposed the RCA cleaning procedure in 1970 [1]. This cleaning solution is prepared based on hydrogen peroxide using sulfuric acid, hydrogen fluoride, ammonia, hydrochloric acid and ultra pure water. To begin with, the liquid mixture (SPM) of sulfuric acid and hydrogen peroxide is used to remove organic impurities in the cleaning process at the temperature of $120 \sim 150^{\circ}$ C. Next, the dilute hydrogen fluoride is used in order to remove the oxide film created by previous process.

	Table 1 Radical g	eneration in RCA	cleaningsolutioms
--	-------------------	------------------	-------------------

RCA cleaning solution	DMPO-OH	ДМРО- СН _З СНОН	OH radical
SPM solution	Detection	Detection	Generation
HPM solution	Detection	Detection	Generation
FPM solution	Detection	Detection	Generation
APM solution	Detection	Non-detection	

Used chemical solution	DMPO-OH	дмро- сн ₃ снон	OH radical
H2SO4	Non-detection	Non-detection	6172903
HCI	Non-detection	Non-detection	entrices
HF	Non-detection	Non-detection	costata
NH4OH	Non-detection	Non-detection	0137133
H2O2	Detection	Non-detection	energia

the table indicates that the radical trapping agent DMPO traps CH₂CHOH radical formed by the reaction between OH radical and ethyl alcohol CH₃CH₂OH.

From this table, it is noted that OH radical is generated in RCA cleaning solutions except for APM cleaning solution. On the other hand, OH radical generation is not found in the chemicals used in wafer cleaning process such as H₂SO₄, HCl, HF, NH₄OH and H₂O₂ itself.

Hydrogen peroxide H₂O₂ and proton H⁺ exactly exists in RCA cleaning solution. Moreover, chemical solutions used in RCA cleaning method such as H₂SO₄, HCl, NH_4OH and H_2O_2 includes the residual impurity Fe as much as the amount of 10+14 ~ 10^{+16} [atoms/L]. It is found that OH radical is generated by Harber-Weiss



Figure 3 RCA cleaning solution

Afterwards, the particles are removed by liquid mixture (APM) of ammonia, hydrogen peroxide and water of $80 \sim 90^{\circ}$ C called SC1. Then, the metal impurity is removed in mixed solution (HPM) of hydrochloric acid and hydrogen peroxide and water of 80 ~ 90°C called SC2. Finally, the oxide film is removed by the dilute hydrogen fluoride solution.

Table 1 shows the radical generation in RCA cleaning solutions using ESR (Electron Spin Resonance) radical measuring system. In this case, DMPO (5,5-dimethyl-1-pyrroline-N-oxide) is used as the radical trapping agent [4]. DMPO-OH as shown in the table 1 means that the radical trapping agent DMPO traps OH radical. And DMPO-CH₃CHOH in



Figure 4 Mechanism of OH radical generation in RCA cleaning solution

Figure 4 shows the generation mechanism of OH radical in acidic RCA cleaning solutions.

Chemical solution	Concentration of Fe [atoms/L]
H ₂ SO ₄	5.790×10 ¹⁵
HCI	3.474×10 ¹⁶
NH4OH	3.474×10 ¹⁶
H_2O_2	1.158×10^{14}
ويرافعون ويراد بمرافعاته فتنافعه فالمحمل فالمتعاط والمتعارين الألا	فالمستحدة ومسرحة والمحد والمحد والمحد والمحافظ والمراجع والمتعاد والمحافظ والمحافظ والمحرور والمحافظ المحافظ ال

Figure 5 Residual concentration of Fe in chemical solution

reaction catalyzing metal ion Fe as shown in Figure 5. By the different experiment, the quantity

of OH radical created in the SPM cleaning solution has confirmed to increase in increasing the ferrous ion in the cleaning solution. Moreover, the generation of the OH radical is confirmed using the ESR system. At the same time, the generation of super-oxide ion O_2^- is confirmed using the ESR system.

Figure 6 indicates the effect of pH value on the generation of OH radical in RCA cleaning solution and the hydrogen peroxide solution of which pH values are controlled by a small amount of each acid.

SPM Cleaning Solution min) 1.50x1015 🗱 HPM Cleaning Solu A FPM Cleaning Solution Number of OH radical [1/ (L. 0 pH was controled by H2SO4 1.00x10¹⁹ ed by HCl pH was controled by HF 5.00x10¹⁸ HQ. ъH Figure 6

Effect of pH value of cleaning solution on OH radical formation

From the viewpoint of OH radical generation, it is clear that the functional water such as the hydrogen peroxide solution of which pH values are controlled by a small amount of each acid, is very similar to that of RCA cleaning solution. This means the possibility of reducing the

consumption volume of chemicals used in the silicon wafer cleaning process.

Ultrasonic Excitation Water

Figure 7 shows the variation of resistivity of ultra pure water with megasonic irradiation time. The megasonic means the ultrasonic wave of the megahertz band, here. In the case of the ultra pure water dissolved sufficiently with both N_2 and O_2 gas, the resistivity of ultra pure water is suddenly changed by megasonic irradiation.



Variation of resistivity of ultrapure water with megasonic irradiation time

This means the quality change of the ultra pure water by megasonic irradiation. Namely, the resisitivity change of the ultra pure water can be caused by the generation of new electrolytes in water. On the other hand, the resistivity change is not found in degassed ultra pure water.

Figure 8 show the generation of the nitric acid ion NO_3^- as a function of the dissolution quantity of air, respectively. Increasing in the sonication time, the concentrations of nitrous acid ion and nitric acid ion are found to increase. The nitrous acid ion NO_2^- is also generated in





the water. This is from the oxidation of NH_3 formed by ultrasonic energy in the water. And the generation of ammonia ion NH_4^+ is also confirmed by another experiment and ion measurement. Moreover, the generation of the hydrogen peroxide in the megasonic

excitation water is also confirmed by measuring H_2O_2 . The generation of OH radical and H atom cause the above-mentioned ion generation from the water by the ultrasonic irradiation.

Figure 9 shows the effect of oxygen and nitrogen concentrations in ultra pure water on the radical generation. In this case, it is adjusted so that the total concentration of O_2 and N_2 in the ultra pure water may become always-constant value of 18 ppm. It is revealed that the generation of the OH radical shows the maximum value within $3 \sim 9$ ppm of oxygen content and $9 \sim 15$ ppm of nitrogen content. On the other hand, it is found that there is no existence of the H atom in the solution at the concentration of oxygen higher than 3.5 ppm. Furthermore, it is noted that the generation of OH radical and H atom from water excited with ultrasonic irradiation is strongly affected by the type of dissolution gas. However, the wafer itself does not affect the OH radical formation in the ultrasonic excitation

water.

Figure 10 shows the effect of the dilute chemical addition in the ultrasonic excitation water on the radical generation. The addition of NH_4OH in the water shows the highest effect on the OH radical generation compared with the other electrolytes.



Figure 10 Effect of dilute chemicals on OH radical generation by Megasonic irradiatio

Figure 11 indicates the estimated reaction path of ion species generation in ultra pure water excited with ultrasonic wave. Ammonia ion NH_4^+ , nitrous acid ion NO_2^- , nitric acid ion NO_3^- and hydrogen peroxide H_2O_2 are found to generate. These chemical species are already confirmed in this study.



Figure 11 Reaction path of ion species generation silicon surface of its orientation (100) is also cleaned by the nitrogen saturated ultra pure water, which is irradiated by the ultrasonic wave. Silicon substrate, of which surface is treated by the ozonized water of $4 \sim 9$ ppm ozone, is used for the sample piece. In the case of using the ultrasonic wave excitation water dissolving nitrogen gas, it is noted that a little roughness and the local ruggedness is on the surface after the cleaning unlike the Figure 12 shows the etching effect of the generated OH radical in the cleaning solution saturated with argon gas on the silicon surface (100). Silicon substrate, of which surface is treated by the ozonized water of $4 \sim 9$ ppm ozone concentration, is used for the experimental sample piece. From this figure, it is noted that the roughness created by NH₄OH of 100 ppm on silicon substrate is etched by megasonic irradiation exactly. The



ultrasonic wave excitation water including argon gas. It can be considered that the oxide film of the wafer surface is not sufficiently removed by the pretreatment. Therefore, it is supposed that the exposed silicon is more quickly etched. The investigation of this cause will be expected for future research.

Figure 13 also shows the variation of silicon surface (100) treated with the ultrasonic excitation water dissolving hydrogen gas. It is clearly seen that the silicon surface treated with 10 % HF solution becomes the smoother





surface after ultrasonic wave irradiation.

Figure 14 shows the variation of the silicon dissolution from the silicon substrate into water, which is excited by ultrasonic wave, with the elapsed time as a function of dissolving gas. At the

same time, the amount of OH radical generation is also shown in the figure as a function of dissolving gas species. The silicon quantity as shown in the figure is the value, which corrected silicon quantity, which remains in the ultra pure water and comes out of the quartz container. Silicon concentration in the functional water is measured using silica-monitor offered by Central Gas Co. Ltd. of Japan. It is noted that the



dissolution quantity of the silicon increases with the elapsed time. This means that the silicon substrate is etched by the effect of megasonic irradiation. It is considered that main cause of the etching is OH radical generated in the water. However, from the figure, in saying, as the generation of the radical is abounding, it is understood that the etching rate is not always high.

Ultraviolet Excitation Water

Figure 15 shows the wavelength distribution of used ultraviolet light that is emitted from the low-pressure mercury lamp. From this figure, it is noted that 185nm of ultraviolet is excluded in the nominal 254 nm ultraviolet lamp.

Figure 16 shows the effect



of the type of dissolving gas in ultra pure water on OH radical generation caused by ultraviolet irradiation. From this figure, it is noted that the irradiation of ultraviolet whose wavelength longer than 254 nm does not generate the active OH radical in ultra pure water that any gas is dissolved. However, as the ultra pure water including a photocatalyst such as TiO_2 particles is irradiated by ultraviolet of wavelength 254 nm, OH radical is drastically



Effect of type of dissolving gas in UPW on OH radical generation by UV irradiation

generated in the ultra pure water that any gas is dissolved. On the other hand, the irradiation of ultraviolet including the wavelength of 185 nm produces OH radical in the ultra pure water that any dissolved gas is controlled. It is also noted that the ranking of dissolved gas that abundantly forms OH radical is in the order of air, nitrogen, carbon dioxide, hydrogen gas and argon gas. The



possessed energy of wavelength of 185 nm ultraviolet is almost same as the bonding energy between oxygen and hydrogen atom of water molecule. Figure 17 indicates the comparison of the production of OH radical and H atom due to the irradiation of ultrasonic wave and ultraviolet of 185 nm wavelength. Generally, the megasonic irradiation will generate the much higher OH radical concentration than that generated by 185 nm ultraviolet irradiation. The ultraviolet

irradiation of 185 nm wavelengths is found to be very effective to generate the H atoms. The remarkable matter is to generate more many OH radicals in the ultra pure water, which is added by ammonia, irradiated with ultrasonic wave.

Ozonized Water

It is well known; ozone is composed of three oxygen atoms, generally existing in a very unstable and reactive state. Recently, due to these unstable and high reactivity, ozone is expected

to play a more important role in various fields such as semiconductor production process, water and wastewater treatment, medical field, food products and food processing, especially environment problem, and so on. The ozone molecule has been composed of three oxygen atoms [5]. The bond length between oxygen atoms of ozone molecule is 0.1278 nm and the bond angle between oxygen atoms of ozone molecule is 116.87 degrees. The ozone molecule has resonance structure as shown in the figure. The ozone molecule shows the polarity, because central oxygen atom is δ +, and because the other oxygen atom is δ - [6]. These are the features of the ozone molecule. The dissolution

$$O_3 + OH^- \rightarrow O_2^- + HO_2^-$$

$$O_3 + HO_2^- \rightarrow 2O_2 + OH^-$$

$$O_3 + OH^- \rightarrow O_2 + HO_2^-$$

$$2HO_2^- \rightarrow O_3 + H_2O$$

$$HO_2^- + OH^- \rightarrow O_2 + H_2O$$
J. Weiss et. al. (1935)

$$O_3 + H_2O \rightarrow OH^- + HO_3$$

$$OH^- + HO_3^- \rightarrow 2HO_2^-$$

$$HO_2^- + O_3^- \rightarrow 2O_2 + OH^-$$

$$OH^- + HO_2^- \rightarrow O_2^- + H_2O$$

G. Akder et. al. (1950)

Figure 18 The decomposition reaction of the ozone.

of the ozone into the water follows Henry law.

Figure 18 indicates the reaction path of the decomposition of the ozone proposed by Weiss J. et al. (1935) [7] and Alder G. et al. (1950) [8]. According to Weiss et al. and Alder et al., the ozone reacts with hydroxyl ion OH and water H_2O in neutrality or alkalinity, and OH radical and hydro-peroxide HOO^{*} or super-oxide O_2^- are generated. In the water (pH = 5.5~5.35), pH value of water is lowered to 4.5 when it dissolves around 20 ppm. The ozone dissolved in the water pulls out the electron from the hydroxyl ion. Then, the ozone is decomposed into oxygen molecule and the oxygen atom. Therefore, it is considered that hydrogen peroxide H_2O_2 is formed by the reaction of oxygen atom with the water. And, it is also considered that the formed oxygen atom reacts with each other to form the oxygen molecule. The hydroxyl ion of the

solution decreases by the reaction between O_3 and OH. And as the hydrogen ion will increase, the solution shows the acidity. And, the dissolved oxygen concentration of the ozonized water will increase due to the generation of hydrogen peroxide and the decomposition of the ozone.

Figure 19 shows the drastic generation of OH radical in the ozonized acidic water. In the ozonized acidic water, the hydrogen peroxide, hydrogen ion and metal impurity of iron coming from the acid added for



controlling pH value of solution. So, it is assumed that the generation of OH radical is caused by Haber-Weiss reaction, which is mentioned before, in the ozonized acidic water. On the other hand, though it is not shown in the figure, the OH radical is not found to generate in neutrality or alkalinity of the ozonized water.

Figure 20 shows the metal dissolution properties to the ozonized water of which concentration of ozone and acetic acid is $5 \sim 6$ ppm and 16.3 ppm, respectively. It is noted that each metal dissolves into the ozonized acidic water as increasing in the cleaning time as shown in the figure. However, the practical ionization order of metal is not same as the order estimated by electrochemical method such as oxidationreduction potential method. It revealed that the practical order of metal dissolving into ozonized acidic water rather depends on the magnitude of work function of metal. From the other



experiment, the metal dissolution into the ozonized acidic water is found to increase with decreasing in acid concentration. It is also found that the active oxygen and oxygen molecule

formed by the ozone decomposition strongly affect the metal dissolution into the ozonized acidic water. Therefore, it is concluded that the metal dissolution into water is necessary to exist proton H^* , oxygen molecule O_2 and oxygen atom O. The O atom and O_2 molecule will be formed by the decomposition reaction of ozone in the functional water.

Figure 21 indicates the confirmation of metal dissolution phenomena mentioned above.

From this figure, it is noted that the metal copper dissolves well into the water dissolving air, which includes the carbon dioxide. This carbon dioxide reacts with water to generate the hydrogen ion immediately. Namely, the solubility condition of metal dissolution would be prepared. The metal dissolution mechanism can be considered from the mentioned above.



Ability of metal dissolution in the carbon dioxide dissolution water Concentration of CO₂ in air saturated water : 0.5214 [ppm]

Figure 22 shows the dissolution

of metals as a function of the dissolving gas species. In this case, the oxalic acid is used for the proton donor. It is noted from the figure that the existence of oxygen molecule and proton in the water promotes to dissolve the metal into the water. Highest dissolution effect is obtained around

the concentration of oxalic acid from 50 ppm to 100 ppm. However, the concentration of metal dissolution begins to decrease beyond the oxalic concentration of 100 ppm. Moreover, the effect of organic acid such as acetic acid and formic acid on the dissolution of metal into the water is also examined. It is noted that both organic acid are very effective for the dissolution of metal into the water under the existence of oxygen and proton in the water.

Hydrogen Dissolved Water

Figure 23 shows the effect of ultrasonic irradiation on the radical generation in ultra pure water saturated by hydrogen. In this case, OH radical is mainly formed in the water. This is because the hydrogen atom generated from the water reacts with oxygen atom O produced by hydrogen peroxide H_2O_2 , which is formed by OH radical induced with





Figure 23 Radical generation by megasonic irradiation to UPW saturated with H₂

ultrasonic irradiation. In the figure, the reducing phenomena of OH radical can be considered due to the quick decomposition rate of the radical trapping agent along with the ultrasonic irradiation time. The effect of addition of ammonium hydroxide NH_4OH on the OH radical generation in the ultrasonic excitation water saturated hydrogen is also examined. The addition of small amount of NH_4OH is found to be very effective for increasing in OH radical generation. By the irradiation time around 6 minutes, the radical generation tends to increase with increasing in the ultrasonic irradiation time. In this region, it is noted that the radical generation rate is a little higher, as the ammonia addition quantity is less. On the other hand, beyond the about 6 minutes of irradiation time, the radical generation rate tends to decrease as the irradiation time increases. The decline of radical generation is high as the ammonia addition quantity is less. This is because the decomposition rate of DMPO adduct, which is formed by trapping OH radical, is higher than the radical generation rate. In either case, it is noted that the effect of a little amount of the ammonia addition in the hydrogen-dissolved water is very high.

Electrolytic Water

It is considered that the pure water without dissolved gas completely is electrolyzed. The water molecule has large dipole moment (1.85 D) of it itself. And, it has high 78.5 dielectric constants. Therefore, the water molecule is dissociating into H⁺ ion and OH ion in the liquid state of room temperature. Using the cation exchange membrane of fluorine, the electrolytic processing is carried out in the current density of 20 mA/cm² or less. In this case, Pt is used for anode (positive electrode) and cathode (negative electrode) electrode. The hydrogen and the oxygen are obtained in the anode and in the cathode, respectively. In this case, the property of the solution is neutral and the value of pH is 7 [9]. And the reactions in each electrode are as follows.

Anode Reaction : $2H_2O - 4e \Rightarrow 4H^+ + O_2$ Cathode Reaction : $4H^+ + 4e \Rightarrow 2H_2$

However, the generation of ozone O_3 is observed in the anode side whether the current density increases or β -PbO₂ is used as the anode electrode for the electrolysis. Reactions are as follows.

Anode Reaction : $3H_2O - 6e \Rightarrow 6H^+ + O_3$ Anode Reaction : $H_2O + O_2 - 2e \Rightarrow 2H^+ + 2e + O_3$ Cathode Reaction : $4H^+ + 4e \Rightarrow 2H_2$

Figure 24 shows the comparison of the OH radical generation of SPM cleaning solution with that of anode cleaning solution. The values of pH of each cleaning solution are controlled by H_2SO_4 . From the viewpoint of radical generation, it is noted that the OH radical generation in

anode water is very similar to that of SPM cleaning solution. So, the anode water can be used as the cleaning solution instead of SPM solution for the removal of metal ion and organic substance. The effect of H_2O_2 concentration in SPM and anode solutions on the OH radical generation is examined in detail. The mixing ratio of sulfuric acid and hydrogen peroxide of SPM and anode water and hydrogen peroxide of anode water is 4 vs. 1 at pH = 1.2. The concentration of H_2O_2 changes from $1 \times$



 10^6 to 1×10^1 mol/L. The OH radical generation increases with increasing in the concentration of H_2O_2 . From the experimental observation, it is noted that the OH radical generation behavior is very similar for each other. So, it is clear that anode water can be used as the removal solution of metal ion and organic substance instead of SPM cleaning solution.

Degassed Water

The deaeration ultra pure water, of which dissolved gas component in the ultra pure water is removed as much as possible, is examined. Dissolution air in the ultra pure water is deaerated to 10^4 Torr. Figure 25 shows the measurement result on the radical generation in irradiating deaeration ultra pure water with the ultrasonic wave. The generation of radical is not observed from the deaeration ultra pure water. However, it is also considered that DMPO of spin trapping agent is destroyed by the deaeration operation. In order to confirm this, the oxygen is dissolved in

the sample and the ultrasonic irradiation is carried out again. As the result, it is confirmed that the reactivity of DMPO had not been lost by the generation of the OH radical as shown in Figure 25. Therefore, it can be said that the



Figure 25 The effect of ultrasonic irradiation on radical generation in degassed ultra pure water

radical is not formed, even if the deaeration ultra pure water is irradiated with the megasonic. This indicates that the existence of the dissolved gas is necessary for the radical generation in the ultra pure water irradiated with the ultrasonic wave.

Cleaning Effect of Each Functional Water

Figure 26 shows the cleaning effect of each of the functional waters [10]. The vertical axis means adhesion quantity of copper and horizontal axis is each of functional waters. It is also clearly known from this figure that ozonized or anode water can remove the copper from the silicon surface.

Figure 27 shows the removal of organic materials (IPA) by solution excited by ultrasonic [10]. The ozonized water, which is added with hydrogen peroxide and irradiated by megasonic, can remove TOC from silicon surface. The functional water can be suitable for silicon surface cleaning rather than RCA cleaning solution from the viewpoint of waste water treatment, reusing of resources. Because the consumption volume of chemicals used for cleaning can be reduced using functional water.







Morita Hiroshi [11] demonstrates to show the actual difference of fine particles removal from the silicon surface between conventional RCA cleaning method (SC1) and the functional water dissolved H_2 with a small amount of NH₄OH addition. Functional water is found to be able to remove fine particles much better than RCA cleaning solution.

CONCLUSION

The function water was examined from the viewpoint of the radical generation, and the following conclusions are obtained.

Ion species and hydrogen peroxide are formed in the ultra pure water by ultrasonic irradiation. (2) It is revealed that the dissolved gas component influenced the generation of OH radical by ultrasonic irradiation. (3) It is found that the generation of OH radical was not observed when the ultra pure water is degassed up to 10^4 ppb and irradiated by the ultrasonic wave. (4) OH radical generation in the hydrogen peroxide solution irradiated by the ultrasonic increases with increasing in the hydrogen peroxide concentration. (5) The generation of the radical by ultrasonic irradiation is not observed in the hydrogen fluoride solution. (6) OH radical generation is promoted in ozone aqueous solution of the lower value of pH. (7) In the cleaning procedure using ultrasonic wave (Functional water cleaning), it is concluded to be very similar mechanism to the conventional RCA cleaning because the active OH radical is formed as same as in RCA cleaning. (8) The wavelength shorter than 185 nm is found to be very effective in order to activate the water by ultraviolet irradiation. (9) It is indicated that the ultraviolet of 254 nm did not have the energy of cutting off the combination of hydrogen and oxygen of water. However, it is possible that floating the photo catalyst, for example, TiO₂ and so on forms the OH radical exactly.

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Single Wafer Cleaning

EFFECTIVE POST-ETCH RESIDUE REMOVAL ON LOW-K FILMS USING SINGLE WAFER PROCESSING

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ABSTRACT

Integrating copper and low-k dielectrics remains challenging but necessary to semiconductor processing progress. Removing post-etch residues from copper and low-k materials is a critical part of this effort. The initial step in this work was to investigate the compatibility of low-k dielectrics with different residue removal chemistries in a "static beaker" setup. The chemical compatibility of the materials was evaluated by observing changes in thickness and refractive index as measured with spectroscopic ellipsometry. Next we tested residue removal efficiency of several of the chemistries on dry-etched 200mm wafers. The wafers were processed in a Semitool® Capsule™ single-wafer processing chamber. Residue removal capability and material compatibility were studied using X-section SEM.

INTRODUCTION

Semiconductor interconnect fabrication is marked by the drive for faster devices and thus smaller geometries which effort has recently led to the introduction of a host of new materials of vastly superior electrical properties but also, in many cases, vastly inferior chemical and physical integrity. Wet-processing steps, once predicted to decline in number, now make up a larger number of steps in the total process flow than ever before as "wet-processing" has moved into a new era of "ultra-clean surface preparation". Drastically tighter process windows and a higher dollar value per wafer are persuading many manufacturers to switch to single-wafer processing for better process control. Thus, for single-wafer post-etch cleaning applications, the need to compete with and even surpass the output of batch systems means that chemicals must act much more aggressively toward complex residues while maintaining a greater selectivity toward a wider array of more sensitive materials, such as copper and porous low-k dielectrics. For the opening of the SiC etch-stop layer onto the underlying copper, the post-etch residues created have a highly complex composition including Cu, CuO, Cu₂O, Si, C, and numerous fluoride. It is critical to the manufacturing process that these residues be efficiently and effectively removed without damage to stack materials. The aim of this project is to compare several single-wafer residue removal chemistries for cleaning efficiency and compatibility. The chemicals are tested on two low-k materials, Black Diamond I (BDI) and porous SiLK v.9 (p-SiLK). BDI is a dense, silicon-oxide-based CVD low-k material with an approximate k-value just under 3.0 and a refractive index (RI) around 1.41, while p-SiLK is a porous, spin-on "ultra-low-k" film of cross-linked polyphenylene with an approximate k-value of 2.2 and a RI of 1.55. The chemicals are identified in Table I according to their respective primary active constituents.

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I able I	: Test Chemicals
Chemical	Primary component
Chem A	N,N-dimethylacetamide,
	Ammonium fluoride
Chem B	Ammonium fluoride (NH ₄ F)
Chem C	Fluorine (< 1%)
Hydrofluoric Acid	Hydrofluoric acid (HF)

Two HF mixtures were used; 0.025v/v% and 0.050v/v%. Each of the tested chemicals is water-soluble, requiring no rinse between the water and the chemical. Aside from initial chemical screening in beaker tests, all wet-processing tests were done on a 200mm single-wafer tool.

1.1

1

CHEMICAL COMPATIBILITY SCREENING EXPERIMENTS

Changes in thickness and RI of blanket low-k films were measured with a spectroscopic ellipsometer (SEN-TECH-801). A wafer sample was exposed to a chemical for 2 or 10 minutes at ±20°C or ±40°C in a "static beaker" setup. A 1-L beaker was filled with 400ml of fresh chemistry for each test (no stirrer used). After treatment, samples were removed, rinsed in DI water (60sec.) and dried in N₂ (±30sec.). Results of the testing are given in Tables II and III. The evaluated chemistry is considered compatible with a particular substrate at the settings tested if the thickness change remains below 5 nm and the RI variation remains below 0.005. Thus, as the data in Table I shows, all chemicals tested exhibited good compatibility with BDI. P-SiLK is compatible with dHF and Chem C with almost no change in thickness or RI.

Table II: Thickness and RI Change, blanket BDI in beaker						eaker		
Cham	Time	Temp	Thickness (nm)			RI@633nm		
Chem	(min)	(°C)	Before	After	Change	Before	After	Change
	2	20	1007.0	1005.7	-1.3	1.420	1.420	0.000
Cham A	10	20	1012.8	1013.1	+0.3	1.420	1.420	0.000
Chem A	2	40	1011.8	1009.7	-2.1	1.419	1.419	0.000
	10	40	1014.3	1014.5	+0.2	1.421	1.420	-0.001
	2	20	1011.1	1014.9	+3.8	1.422	1.421	-0.001
Cham D	10	20	1015.4	1016.2	+0.8	1.423	1.422	-0.001
Cnem B	2	40	1002.0	1004.5	+2.5	1.422	1.420	-0.002
	10	40	1011.4	1015.0	+3.6	1.422	1.421	-0.001
	2	20	239.7	239.0	-0.7	1.425	1.425	0.000
Cham C	10	20	232.4	230.1	-2.3	1.426	1.424	-0.002
chemic	2	40	229.4	228.9	-0.5	1.430	1.428	-0.002
	10	40	232.3	228.8	-3.5	1.430	1.429	-0.001
HF	2	20	991.4	993.7	+2.3	1.421	1.422	+0.001
(0.025)	10	20	997.4	996.1	-1.3	1.423	1.422	-0.001
HF	2	20	1002.2	1001.7	-0.5	1.421	1.422	+0.001
(0.050)	10	20	1007.9	1009.4	+1.5	1.423	1.423	0.000

I DI CI

Table III: Thickness and RI Change, blanket p-SiLK in beaker^t

Cham	Time	Temp	Thickness (nm)			RI@633nm		
Chem	(min)	(°C)	Before	After	Change	Before	After	Change
	2	20	351.8	350.0	-1.8	1.494	1.494	0.000
Cham A	10	20	351.8	349.0	-2.8	1.494	1.496	0.002
Chem A	2	40	351.8	345.0	-6.8	1.494	1.503	0.009
	10	40	351.8		-	1.494	-	_
	2	20	350.1	356.6	6.5	1.496	1.528	0.032
Cham B	10	20	350.1	360.7	10.6	1.496	1.553	0.057
Chem B	2	40	350.1	360.8	10.7	1.496	1.538	0.042
	10	40	350.1			1.496	_	
	2	20	175.5	175.5	0.0	1.547	1.553	+0.006
Chem C	10	20	175.5	174.5	-1.0	1.547	1.550	+0.003
Chemic	2	40	175.5	171.1	-4.4	1.547	1.544	-0.003
	10	40	175.5	173.7	-1.8	1.547	1.551	+0.004
HF	2	20	350.7	351.6	0.9	1.491	1.491	0.000
(0.025)	10	20	350.7	352.0	1.3	1.491	1.490	-0.001
HF	2	20	350.7	351.6	0.9	1.491	1.491	0.000
(0.050)	10	20	350.7	352.0	1.3	1.491	1.490	-0.001

^tPre-process values represent a single initial measurement.

Chem B caused a significant increase in thickness and RI, possibly indicating a swelling of the porous material due to absorption of chemical. Here, too, a treatment of 10 minutes/ 40° C completely removes the p-SiLK layer.

POST ETCH RESIDUE REMOVAL

Single damascene test wafers were prepared as follows:

Stack, bottom-up

· Stack, bottom-up

Etch Process

- Etch Process
- 1000nm Cu, 50nm SiC, 275nm BDI, 9nm SiO₂
- \bullet Low-k etch in Lam 2300 Exelan chamber using Ar/CF_4/CH_2F_2/O_2
- \bullet SiC open in Mattson Highlands chamber with CF_4/H_2 100/100 plasma
- \bullet 1000nm Cu, 50nm SiC, 250nm p-SiLK, 50nm SiC, 150nm SiO_2
- \bullet Oxide open in the hardmask using Ar/CF_4/CH_2F_2/O_2
- \bullet SiC open using Ar/CF_4/CH_2F_2/N_2
- Low-k etch using N2/H2
- \bullet SiC open in Mattson Highlands chamber with CF_4/H_2 100/100 plasma

Single Wafer Processing

• BDI

• p-SiLK

All wet processing described herein was performed in a Semitool[®] Capsule[™] singlewafer surface preparation chamber. chamber The encapsulates the wafer within a 'micro'-processing environment and is made to spin during process at a selectable speed, likewise spinning the wafer. Process chemistry is delivered to the center of the front side of the wafer, moves across the wafer surface to exit at the edge where it can be reclaimed for continued use. Next, DI water is delivered to both sides of the wafer, followed by IPA-vapor-assisted drving of both wafer sides. Table IV contains the specific recipe used in these tests. Table V contains the matrix of residue removal tests performed.

Table IV: Post-Etch Residue Removal Cleaning Recipe

Step	Action	Temp (°C)	Time (sec)	RPM	DI	N ₂ /IPA	Chem
1	Spin	25	5	500			
2	Chem	25/40	60/120	500			Т
3	Rinse	25	45	600	TB		
4	Dry	19	45	1800		TB	

T: Top delivery

TB: Top and Bottom delivery

Tuore (Terreneting (80)/Time (20)						
Film	Chemical	Temperature (°C)/Time (sec)					
*	Chemiean	25/60	25/120	40/60	40/120		
BDI	Chem A	Х	X	Х	X		
	Chem B	Х	X	Х	X		
	Chem C	Х	Х	Х	X		
	HF (0.025)	Х	X				
	HF (0.050)	Х	X				
p-SiLK	Chem A	Х	X				
	Chem B	Х	X	Х	X		
	Chem C	Х	X	Х	X		
	HF (0.025)	Х	X				
	HF (0.050)	Х	X				

Table V: Post-Etch Residue Removal Test Matrix

<u>Pre Process.</u> Figures 1-10 contain SEM images of single damascene structures in BDI and p-SiLK. The SiC-open process was intentionally tuned to produce the large amounts of residues seen in Figures 1 and 2. For both wafer types, copper pads are completely covered with residues. BDI sidewalls exhibit little if any residue, while large nodules are clearly visible on sidewalls of p-SiLK. Residues in trenches are heavy on the BDI wafers, only more so on p-SiLK. BDI vias have light residues on the sidewalls (Fig. 1), while the bottom residues closely resemble those of copper pads. The p-SiLK sidewall residues manifest as large nodules, bottom residues as a thick brittle film. The extreme amount of residue provides a 'worst-case' scenario for testing. (Note: the roughness of the BDI-stack surface is due to an upstream process and unrelated to cleaning.)



Figure 1. Structures in BDI before Post-Etch Clean



Figure 2. Structures in p-SiLK before Post-Etch Clean

<u>Chemistry A.</u> Chem A demonstrates low compatibility with copper. Figure 3 clearly illustrates severe copper attack even at 25°C/60-sec. At 40°C, residues are seen on the copper and sidewalls. However, a follow-up dip in Chem A, followed by a rinse/dry, was sufficient to remove them (picture not shown). After a delay of several days, these recleaned samples were examined again under SEM and the 'residues' had returned. Such "re-growth" of residues has been examined before (1).



Figure 3. Structures in BDI following clean in Chem A

With p-SiLK, results at 25°C indicate some residue remaining at the bottom of the vias; copper attack is clearly visible in narrow trenches; and low-k sidewalls still exhibit nodules of residue (quite possibly the same "re-grown" residue seen with BDI). Copper attack was also clearly visible in open copper areas. One can see in Figure 4 that the dielectric stack is significantly undercut.



Figure 4. Structures in p-SiLK following clean in Chem A

<u>Chemistry B.</u> Using Chem B on BDI (Fig. 5), all parameter combinations tested produced clean wafers in good condition. There are some indications of small amounts of remaining residue after the 25°C/60-second process. Sidewalls look very clean with no indication of attack. At 40°C, one sees the indication of undercut at the edge of the open copper field. (Note: the textural difference of copper near to the dielectric stack is due to the well-understood phenomenon known as "micro-trenching" that occurs during SiC open (2).)



Figure 5. Structures in BDI following clean in Chem B

For p-SiLK, Chem B was again a strong and compatible cleaner (Fig. 6). At 25°C and 60-sec, residues remain in narrow trenches. In all other tested settings, the wafers appeared clean with no strong indications of low-k or localized copper attack though, at the higher temperature, one begins to see evidence of the copper etching. Smaller vias appear sometimes to have a white 'halo' around the upper edge. This effect is not fully understood and may or may not indicate residues. One can still clearly see texture in the cleaned vias, evidence of the pores present in this material and another indication of complete cleaning.

Electrochemical Society Proceedings Volume 2003-26



Figure 6. Structures in p-SiLK following clean in Chem B

<u>Chemistry C.</u> Unfortunately, problems with processing and analysis of the BDI samples in Chem C were skewed by an as yet unexplained error and thus are not included here.

For p-SiLK, however, Chem C provided very clean copper surfaces including those at the bottoms of small vias, even at 25°C/60-sec. At this lowest setting, sidewall residues are still present, as seen in the large vias in Figure 7. However, higher temperature and longer processing time appear to have provided clean copper and dielectric surfaces with no significant attack. Evidence of slight undercutting is seen.



Figure 7. Structures in p-SiLK following clean in Chem C

<u>Dilute HF at 0.025%v/v</u>. On BDI, we again see re-grown crystals on open copper surfaces, as seen using Chem A. Otherwise, the chemistry has efficiently removed the bulk copper surface residues and no via sidewall polymers are observed.



Figure 8. Structures in BDI following clean in Dilute HF at 0.025%v/v

Cleaning of p-SiLK with 0.025%v/v HF appears to have been efficient and, oddly, shows no indication of re-growth of residues even though the delay between cleaning and SEM analysis was the same as for BDI. Trenches in p-SiLK appear to have been completely cleaned. Etching of copper is evident after 25°C/120-sec where, in pictures of copper fields, undercutting of the stack is seen.



Figure 9. Structures in BDI following clean in Dilute HF at 0.025%v/v

<u>Dilute HF at 0.050%v/v</u>. The 0.050%v/v was far too concentrated for this process causing gross etching of copper and delamination of dielectric stack. Figure 10 shows clearly that copper etching in vias is greater where the SiC contacts the copper.



Figure 10. Structures in BDI following clean in Dilute HF at 0.050%v/v

ETCH RATES OF PLATED COPPER

The etch rates of electroplated copper in the various chemicals are determined using the same recipe described in Table 3. Ten minutes of chemical delivery was used to provide a significant etch depth for accurate determination of rate.

The measured etch rate of copper for the various chemicals matches closely with the observations of copper attack made in the SEM photos above. Chem A and 0.05v/v% udHF, which exhibited copper attack in residue removal testing, are shown here to have very high etch rates for copper, while the chemicals that exhibited limited or no attack of metal also show low etch rates (see Figure 11).

Electrochemical Society Proceedings Volume 2003-26



Figure 11. Etch Rate of Copper

CONCLUSIONS

Chemistry A shows attack of copper even at low temperatures and shows inefficient cleaning even at high temps. Also "re-growth" of residues is seen after time (this may be preventable). Chemistry B causes some significant increases in refractive index and in thickness. However, this chemical, according to SEM analysis, appeared to clean very well, though it did exhibit a significant copper etch rate. Of the commercial chemistries tested, chemical C showed the best combination of compatibility and cleaning efficiency. The copper etch rate was negligible. Dilute HF 0.05v/v% was too strong. The 0.025v/v% solution cleaned well. "Re-growth" of residues occurred on BDI samples but, strangely, not on the p-SiLK samples. The copper etch rate was significant. It is possible that a more dilute mixture could maintain efficiency of cleaning but reduce the copper etch rate.

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Electrochemical Society Proceedings Volume 2003-26

Aqueous Single Pass Single Wafer Al/Via Cleaning

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Abstract

We have developed a dilute aqueous chemical clean for the BEOL Al interconnect technology. This can be used by the DRAM and Flash memory makers and for the last step (bonding pad etch) of the logic device makers. The new clean uses a mixture of bulk chemicals, and is dilute enough so that it can be used in a single pass mode. This provides greatly enhanced process control (e.g. consistent CD control). We also have shown greatly improved particle removal and defect level performance due to single wafer processing.

Introduction

Cleaning operations can be broadly divided into 2 different categories: post patterning cleanings and pre-deposition cleanings. In the BEOL most cleaning operations are post-patterning steps. Historically post patterning cleaning steps included resist strip and clean. This was originally done in the front end with a Piranha clean (H_2SO_4/H_2O_2). This mixture which strips resist efficiently and economically is not compatible with metallic layers and therefore in the BEOL historically solvents were used to strip photoresist. A whole crowd of proprietary mixes were introduced. Most of these were based on a solvent matrix with an amine, which is the active component. Later on, dry oxygen plasma ashing took over the resist strip function from the wet chemicals, but the post ash cleanup remained largely unchanged. In the BEOL the same proprietary mixes based on solvents kept in use, even though the basic requirement had shifted from resist strip to post-strip residue removal.

In this work, we demonstrated that an aqueous solution can be used as a cost effective replacement for expensive proprietary solvents for post-strip residue removal in the BEOL. In this paper, an Al technology is chosen to demonstrate the feasibility of this approach. Al interconnect technology is still being used for memory devices and as the last layer (bonding pad layer) of a typical Cu interconnect scheme.

Methodology Used

In an Al interconnect scheme, there are 2 post-patterning cleanups: the post Al etch and the post via cleans. In both cases we rely on dry oxygen plasma to strip the photoresist and leave the wafer with only post strip residues to be cleaned. In the post Al etch case, most of the residues are completely inorganic, composed of Al and Si oxides. These can be removed by a selective etchant that dissolves these oxides. The mixture chosen uses common inorganic chemicals. We chose for a dilute aqueous mixture to remove these residues. We added hydrogen peroxide to the mix to protect the Al metal from being etched. A similar chemical approach was originally developed by David Rath et al. [1] at IBM. At IBM this approach was developed for a recirculated wet bench. At first, we modified the chemistry to make the cleaning efficient for short exposure times, necessary for single wafer applications. We also needed to develop a

Electrochemical Society Proceedings Volume 2003-26

process for post via patterning. After via patterning and O_2 plasma dry ash, the residues are different from those following Al patterning. The residues after via patterning contain much less metal oxides and contain more C containing polymers. These polymers are on top of the oxide and are harder to remove with a pure sulfuric or acid based chemistry. Therefore, we devised a new way of using this chemistry in a single pass mode. In order to do that, we needed to overcome 3 major obstacles. The chemicals used should be inexpensive chemicals available in bulk, the amount of chemicals used per wafer should be less than 50 cents per wafer for post via clean and less than 25 cents per wafer for post Al clean and finally, the dilution of the chemicals at point-of use needed to be flexible and were not to result in a temperature increase upon dilution. The novel approach that allowed us to achieve these objectives was to pre-mix bulk chemicals down to a slightly lower concentration in order to release all the intrinsic heat of mixing. This was the first time ever that a process for Al line patterning and via patterning was developed that can be used in 1 single wafer tool and with single pass chemistry.

Data

At first we developed the process for cleaning Al lines. The Process development started with a mixture of $H_2SO_4/H_2O_2/H_2O$. This mixture was chosen because it covers the Al with a protective layer of oxide while dissolving Al oxide residues. In this way the oxide gets continuously removed at the outer edge while new oxide gets grown on the Al metal. Since the Al oxide grown on the Al is relatively dense, the Al etch rate will be very small, whereas less dense Al oxide residues on the sidewall of the photoresist will be dissolved very quickly. In order to make this mixture even more efficient at removing residues, we have added HF to this mixture. It should be noted that the Al etch rate is dependent on the initial state of the Al surface. The Al etch rate should be measured on virgin Al wafers or on Al wafers after a O_2 dry ash. When using the same Al wafer multiple times, the etch rate will increase for subsequent wet etches.



Figure 1. Photoresist Residue cleaning after Al etch and photoresist ash with a 60s exposure of a mixture of H₂SO₄/H₂O₂/H₂O/HF at roomtemperature.
The Al clean process result on patterned wafers after dry etch and ash is seen in fig. 1. The photoresist residues are completely removed after 60s exposure.

Next we optimized the post via etch clean process. The residues after the via etch are different from the residues after Al etch, since the etch plasma is different. The residues after the via etch contain much more polymers, since the etch gases for via etch are fluorocarbons. We optimized the post via , which is shown in fig. 2.

Post Oasis Wet Clean



After Via etch and Ash

Figure 2. Photoresist Residue cleaning after via etch and photoresist ash.

We also optimized the particle performance of this process. The particle removal efficiency is greatly enhanced by the use of megasonics. This is shown in fig. 3. For megasonic power levels of 500W or more >80% particle removal efficiency is obtained. This was measured by contaminating the wafers with 0.1 µm Si particles and measuring the cleaning efficiency.



Figure 3. Photoresist Residue cleaning after via etch and photoresist ash.

Solutions

This is the first time a single pass aqueous single wafer clean has been developed for the Al and via clean. One of the difficulties encountered were the viscous nature of the Sulfuric solution. This mixture contains more particles than other aqueous chemicals and because of its viscosity is more difficult to filter. We also employed the megasonics for rinsing the sulfuric. After these changes the final defect count was as shown in fig. 4.



Figure 4. Final Particle count >0.16µm on a 50 wafer run.

Conclusions

The process developed is a marked improvement over the current processes and equipments used in the industry for Al and via cleaning. It is based on a dilute aqueous chemical clean and can be used in Al interconnect and Al bonding pad cleaning. The new clean uses a mixture of bulk chemicals, H2SO4, H2O2 and HF and is dilute enough so that it can be used in a single pass mode.

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Electrochemical Society Proceedings Volume 2003-26

IMPROVED RINSING EFFICIENCY ON POST-ETCH RESIDUE WET CLEAN FOR CU/LOW-K DAMASCENE STRUCTURES

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ABSTRACT

Increased rinse temperature and use of megasonic agitation were shown to improve rinse efficiency for single wafer BEOL post etch/ash cleans. Blanket wafers were used to test particle performance, material loss, copper oxide thickness and copper roughness. Contact resistance was evaluated using 0.2um vias of varying pitch. Use of increased rinse temperature and megasonics was shown to decrease rinse times from 90 to 30s without negative affecting performance. The reduced rinse process was compared with both the single wafer and batch spray PORs.

Keywords: Hot DI Water, Rinsing, Megasonics, Low-k, Copper

INTRODUCTION

Single wafer wet clean systems have been used for post CMP clean, wafer backside treatment and etch back applications for many years. However, its use for back end of line (BEOL) post-etch residue removal applications have only gained limited acceptance. Processing times of less than 3 minutes per wafer will be necessary to achieve acceptable throughput levels. Typical semi-aqueous chemistries for BEOL post-etch residue removal generally require at least 1.5 to 2 minutes of rinsing, greater than 50% of the acceptable total process time. Methods to improve throughput include: multiple chamber systems, modified chemistries and use of acoustic energy.

Although hot water is commonly used for front end of line (FEOL) wet cleans to improve rinse efficiency for piranha and H_3PO_4 , this has been generally avoided for BEOL because of concern for metal corrosion. Under some conditions, increased rinse temperature has been shown to accelerate copper corrosion [1]. This study evaluated using increased rinse temperature with megasonics to determine if the corrosion problem can be avoided while still maintaining the throughput benefit.

EXPERIMENTAL

Single wafer cleans were performed in a Verteq Goldfinger Mach2. ST250[™] was the post etch residue removal chemical. For part 1 of the study, silicon dioxide, low-k (Coral[™]) and copper blanket wafers were used to evaluate the impact of rinse temperature on particle performance, film loss, surface roughness and copper oxide

Electrochemical Society Proceedings Volume 2003-26

thickness. Dielectric film thickness measurements were made with an Optiprobe on a 49 point polar co-ordinate measurement pattern. Copper surface roughness changes were measured with a Digital Instruments Atomic Force Microscope (AFM). Rinsing effectiveness and copper oxide growth was measured using Auger Analysis. Based on the results of part 1, optimized clean recipes with heated DI rinsing were determined. For part 2, the optimized recipes were evaluated using copper/low-k (CoralTM) dual damascene test structures with 0.2um via chains (one million via at 1:2, 1:3 and 1:4 pitch). Contact resistance yield performance for the new clean recipes was determined. Resistance measurements were done with a Karl Suss probe station. Polymer removal effectiveness was determined by cross section via inspection with FESEM micrographs.

For part 1, the cleaning process recipe was 60s of ST250 at 45°C with 100W megasonic agitation, followed by a water rinse with 100W megasonics. The rinse water temperature and time were varied. For part 2, the ST250 time was reduced to 50s and the rinse was 15s at 45°C, followed by 15s at room temperature. Megasonics was used during both the clean and rinse portions of the recipes.

RESULTS AND DISCUSSION

Effects of DI Rinse Water Temperature and Rinse Time on Particle Performance:

Following the ST250 application, water rinse temperatures between room temperature (RT) and 60°C were evaluated. Megasonic agitation was used during the rinse. Blanket SiO_2 wafers that were rinsed for 60 seconds with RT DI water showed poorer performance when compared to a 90 second rinse (Figure 1). This was due to residual ST250 that could not be removed by 60 seconds of RT DI water rinsing. Extending the rinse time to 90s removed the ST250 and therefore produced much better particle results.

Particle performance improved as the DI water temperature increased for the 60s rinse experiments. This could be due to the higher solubility of ST250 or improved megasonic performance at increased temperatures. However, when the wafer was rinsed for 90sec at 60° C, an increase in defects was observed. This is assumed to be some adverse surface changes to the SiO₂ [2,3]. This same effect was seen when wafers were exposed to 90sec of hot DI water without first exposing the wafers to ST250 treatment. The wafers were subsequently treated with a 3min APM (ammonia peroxide mixture) with 100W megasonic at room temperature. The defects could not be removed, indicating either an unremovable defect or a SiO₂ surface change which appears as a defect on the KLA-Tencor SP1. Defects were unable to be located with AFM and defect review SEM.

The same ST250 rinse tests were used to determine the impact of megasonics on rinse performance. Shorter rinse times (30s) were used and rinse temperature was evaluated for splits with and without megasonics. As with the previous tests, reduced defects with increased temperature was observed. These tests also demonstrated a significant improvement when rinsing with megasonics (figure 2). The large difference between with and without megasonics was seen at all temperatures.



Figure 1 - Impact of rinse temperature and time on ST250 rinsing



Figure 2 - Impact of megasonics on ST250 rinsing

Effects of DI Water Rinse Temperature on Coral, Silicon Dioxide and Copper loss:

Film thickness loss when measured using heated rinse water on blanket SiO₂, Coral and copper wafers. Wafers were exposed to ST250 (1,3 and 10 min at 45°C with 100W) and then rinsed (RT and 60°C for 90s with 100W).

For SiO_2 and Coral, the ST250 exposure time and rinse temperature had no significant impact on the film loss. However, copper loss was 50-200% higher when using 60°C rinse water as compared to room temperature (figure 3). This could be due to temperature increase in the remaining ST250 when transitioning from chemical dispense to hot DI water rinse.

29



Figure 3 - Copper loss at varying ST250 exposure time and DI water rinse temperature.

Effects of DI Water Rinse Temperature on Copper Surface Roughness:

Table 1 shows the copper surface roughness for RT and 60°C rinsing. There was some increase in copper roughness with increased rinse temperature. It is likely due to the same reason as the increase in copper film loss. Increase in ST250 temperature when transitioning from chemical dispense to hot DI water rinse is a likely cause.

Split purpose	Clean conditions	Rinse conditions	Copper roughness (RMS)
control	none	none	8.5 ± 0.5 nm
RT rinse	ST250, 45C, 60s	RT, 90s	$10.3\pm0.5 nm$
60C rinse	ST250, 45C, 60s	60C, 90s	$11.0 \pm 0.8 nm$

Table 1 - Copper roughness at different DI water rinse temperature.

Copper Oxide Re-growth on Copper Wafers:

Auger analysis with depth profiling on blanket copper wafers was used to estimate the copper oxide thickness present after 60s of ST250 followed by 90s of rinsing (RT and 60°C). Auger analysis of the control wafers (untreated blanket copper) showed copper oxide thickness of 20-30Å. For both RT and 60°C rinse, the copper oxide thickness was 10-15Å. Therefore, rinse temperature did not have an impact on the copper oxide regrowth. Based on our earlier copper loss data, we could assume that any copper oxide that was originally present would have been removed by the 60 seconds of ST250 exposure. The copper oxide that was detected on these samples was the result of re-

30

oxidation during the rinse step or exposure to the air which did not appear to have been accelerated significantly over 90 seconds of rinsing with 60°C DI water.

Recipe Optimization

The rise in ST250 temperature during transition from chemical exposure to hot DI water rinse presumably increased the copper loss and surface roughness on un-patterned wafers. Therefore, the final rinse strategy was to use an initial short (< 15s) 60°C DI water rinse cycle to remove the bulk of the ST250 residue followed by another short (< 15s) RT DI water rinse cycle. This minimizes direct exposure of the hot DI water to the copper. Particle performance of less than 20 adders with very tight control over 20 continuous runs was still maintained with the new rinse scheme. Rinsing effectiveness verified by Auger analysis of the carbon content on un-patterned copper wafers showed equivalent performance when compared to processing with a 10 minute rinse in a conventional spray processor using cold DI water.

Although, the increased ST250 temperature should increase the chemical's post etch polymer removal efficiency and therefore shorter process times can be used. The ST250 exposure time was also reduced by 15%. Figure 4 shows a typical cross sectional SEM micrograph of vias after cleaning with the newly optimized recipe. The post etch polymer residue could still be removed despite shortening the ST250 exposure time.

Patterned wafers with 1 million via chains at 1:2, 1:3 and 1:4 were used to evaluate the new wet clean recipe with 60°C rinse versus the current single wafer and batch spray tool PORs.



Figure 4 – X-section SEM of 0.2um via at 1:4 pitch after wet clean with optimized recipe

Via Chain Resistance and Via Chain Resistance Yield Comparison

The contact resistance of the 1 million via chains at 1:2 pitch (figure 5) was comparable among the three splits as shown in table 2.

		Clean			Rinse			
Split #	Split purpose	Chem	Temp	Time	Meg	Temp	Time	Meg
1	Single wfr (new process)	ST250	45C	50s	yes	60C	30s	yes
2	Single wfr (POR)	ST250	45C	50s	yes	RT	90s	yes
3	Batch spray (POR)	ST250	30C	10 min	no	RT	10 min	no

Table 2 - Contact resistance splits.

Contact resistance was between 1.1 ohm and 1.4 ohm. The contact resistance spread for each test split was also comparable. The largest difference was observed at 1:3 and 1:4 pitch (figures 6 and 7). Via resistance spread was comparable between split 1 and 2, but poor for split 3 (batch spray). Figure 8 shows the 1 million via chain resistance yield at 1:4 pitch. Test split 1 and 2 did not show obvious difference in the via chain contact resistance yield for resistance of less than 2.20hm; more than 80% yield was achieved in these two test splits. Test split 1 did achieve the highest yield for resistance. A possible reason may be the less efficient cleaning or rinsing due to absence of acoustic agitation. Hong Lin et al [4] have shown from simulations that the use of acoustic energy improves chemical penetration into deep trenches/ via. Better contact resistance yield results for splits 1 and 2 incidates that acoustic agitation plays a role in improving the cleaning performance.





Fig 6 - via contact resistance for 1:3 pitch





Fig 7 - via contact resistance for 1:4 pitch



CONCLUSIONS

It has been demonstrated that under the right conditions, 60°C DI water can be used to improve rinsing efficiency for BEOL cleans without a negative impact. The increased temperature along with megasonic agitation allowed rinse time to be reduced from 90s to 30s. Performance was verified by blanket wafer tests and with 0.2um contact resistance data.

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Electrochemical Society Proceedings Volume 2003-26

SINGLE WAFER WET CLEANING BASED ON SHORT CYCLE TIME, AMBIENT TEMPERATURE AND A SMALL AMOUNT OF CHEMICAL

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For recent further requirements, a short cycle time, reductions of oxide loss and chemical consumption are required for wet cleaning. We found that a two-step process, SC-1 10 sec \rightarrow HF/HCl 10 sec, could improve metal removal efficiency in comparison with one-step processes. In order to improve particle removal efficiency, the two-fluid spray, NanosprayTM, was employed on the first SC-1 step of the two-step process. In addition, the NanosprayTM also achieved low chemical consumption. In this study, we have demonstrated that the two-step cleaning process has the features of a short cycle time, small oxide loss and low chemical consumption for single wafer cleaning.

INTRODUCTION

The RCA cleaning processes have been used more than 30 years in the batch cleaning process [1]. Over the past two decades, several new approaches have been proposed aimed at cost-effectiveness and better cleaning efficiency such as addition of chelating agents [2,3,4,5]. However, those approaches were still based on the RCA cleaning, which causes the drawback of elevating chemical temperature.

Recently, single wafer cleaning attracts much attention due to the reduction of TAT, the prevention of cross-contamination and nm-size particle removal [6]. However, an effective process has not been proposed except for that of Funabashi et al [7].

For recent further requirements, a short cycle time, reduction of oxide loss and chemical consumption are necessary for wet cleaning. Thus, the most efficient single wafer cleaning process, which includes the above features has not yet been established.

In this study, we developed a new single wafer cleaning process, especially for FEOL. As a single wafer spin cleaning system, we employed MP-2000TM (for 8 inch) manufactured by Dainippon Screen. From various experiments, we found that a chemical consisting of very diluted HF for etching and HCl for prevention of metal re-adsorption is compatible with the process for the reduction of the oxide loss and the metal removal efficiency. In order to improve metal removal efficiency further, we focused on the effect of the chemical combination. For the purpose of improving the particle removal efficiency for the two-step process, we adopted the new two-fluid spray, NanosprayTM. It has both features of particle removal and low chemical consumption. Based on the metal and particle removal results, we have demonstrated that the two-step cleaning process at ambient temperature consisting of "SC-1 with NanosprayTM 10 sec \rightarrow HF/HCl 10 sec" meets the demand of single wafer cleaning.

EXPERIMENTAL

Sample and chemical preparation

In order to prepare intentionally contaminated wafers for this study, *p*-type (100); 200 mm wafers were immersed in a contaminated SC-1 solution (NH₄OH:H₂O₂:H₂O = 1:1:5) at 60°C. We controlled metal contamination levels up to 1×10^{12} atoms/cm² by the addition of the standard solution of Fe and Ni ions, because the target of our process is FEOL, and we thought of their contamination level to be below 1×10^{12} atoms/cm². These procedures were following the IAP method [8]. In the cases of Cu and Al contamination level. Therefore, we applied the spin coat method for Cu and Al contamination [9].

In order to measure particle removal efficiency, particle challenge wafers were prepared by a spin coating method using silicon nitride (Si_3N_4) and a polystyrene latex (PSL; 0.19 µm) sphere. We chose Si_3N_4 particles because they are a common material in wafer processing lines and much more difficult to remove them from the silicon surface than the PSL spheres. The number of both Si_3N_4 and PSL particles was controlled to approximately 5000 counts per wafer.

An SC-1 solution was prepared by mixing deionized water (DIW) with H_2O_2 (30%) and NH₄OH (29%). The volume ratio was NH₄OH: H_2O_2 : $H_2O = 1:1:100$. An HF/HCl solution was consisted of HF (50%) and HCl (35%), and the standard volume ratio of HF/HCl was HF:HCl: $H_2O = 1:40:200$. SC-1 and HF/HCl solutions were kept at ambient temperature and 23°C respectively.

Instrumental analysis and Equipment

The surface metal concentration after cleaning was determined using total reflection X-ray fluorescence spectrometer (TXRF). For analysis of aluminum, Inductively Coupled Mass Plasma Spectrometer (ICP-MS) was applied. TXRF measurements were performed on Technos TREX-630S instrument, operated with a W anode at 40 kV and 40 mA. The incident angle was 0.05 rad. The instrument for ICP-MS was a SEIKO SPQ-9000. The number of particles on the wafer larger than 0.12 μ m was detected with KLA/Tencor Surf Scan SP1-TBI. The surface roughness of the silicon wafer was measured by Atomic Force Microscopy (AFM), the instrument was Digital Instruments NanoscopeIIIa. Etching amount measurements were performed at Rudolph CALIBER 300.

Single wafer cleaning was performed by MP-2000TM manufactured by Dainippon Screen (DNS). It achieves a watermark-free process without isopropyl alcohol (IPA). The chemicals and DIW were dispensed onto the rotating wafer from the same nozzle.

Two-fluid spray, NanosprayTM

A two-fluid spray attracts much attention for removal of small particles [10]. In this study, we employed the two-fluid spray NanosprayTM as a new spray-cleaning tool. Spray is created in the mixing nozzle by supplying the chemical (an SC-1 solution in our study) and high flow rate nitrogen gas simultaneously. The nozzle scans at a close distance to a rotating wafer at the rate of 40 mm/sec. Nitrogen gas accelerated the chemical in the mixing nozzle to deliver very fine mist against the wafer surface. Due to the impact power of the spray hitting the wafer surface, particles can be removed effectively.

RESULTS AND DISCUSSION

Metal Removal Efficiency

Figures 1 show the metal removal efficiency for one-step and two-step processes. The lines coming across the columns show the detection limits at TXRF for each metal. Figure 1A (b, c, d) shows metal removal efficiency of one-step processes; SC-1 10 sec, HF 10 sec and HF/HCl 10 sec respectively. It was found that these one-step processes couldn't remove target metals completely. On the other hand, two-step processes consisting of alkali and acid lowered the concentrations of target metals to under the detection limits (Figure 1A (e, f)), and it indicated that the SC-1 10 sec \rightarrow HF/HCl 10 sec process is especially effective on metal removal (Figure 1A (f)). In order to confirm the effect on temperature of the SC-1 solution, we examined it under the condition of SC-1 at 80 °C. Figure 1B shows that iron still remains over the detection limit in spite of applying SC-1 at 80 °C. Therefore it clearly shows the effect of temperature for metal removal.

We selected HF/HCl for an acid instead of SC-2 in the second step. In our two-step process, HF plays the role of slight etching and HCl works to prevent re-adsorption of metals. In order to optimize the HF and HCl concentration ratio in the HF/HCl solution, we investigated the effect of HCl concentration on metal removal. Figure 2 shows the metal removal efficiency on the one-step process of HF/HCl. Figure 2 (f) shows that higher HCl concentration made copper removal easier due to the effect of HCl in preventing re-adsorption of copper. Though copper still remained after the one-step process, it could be removed by applying the two-step process (Figure 3). In Figure 3(b), copper still remained over the detection limit without HCl. However, copper removal efficiency was improved drastically by the addition of HCl (Figure 3 ($c \sim f$)).



Figure 1A: The metallic contamination on the surface for different cleaning processes; (a) initial metal contamination, (b) SC-1(NH₄OH:H₂O₂:H₂O = 1:1:100) at R.T. 10 sec, (c) HF(HF:H₂O = 1:240) 10 sec, (d) HF/HCl(HF:HCl:H₂O = 1:40:200) 10 sec, (e) SC-1 at R.T. 10 sec \rightarrow HF 10sec, (f) SC-1 at R.T. 10 sec \rightarrow HF/HCl 10 sec. Figure 1B: (a) Initial metal contamination, (b) SC-1(NH₄OH:H₂O₂:H₂O = 1:1:100) at 80 °C 10 sec \rightarrow HF/HCl(HF:HCl:H₂O = 1:40:200) 10 sec.



Figure 2: The dependence of the remaining metallic contamination on HCl concentration for HF/HCl 10 sec processes; (a) initial metal contamination, (b) $HF(HF:H_2O = 1:240)$, (c) $HF/HCl(HF:HCl:H_2O = 1:2.4:237)$, (d) $HF/HCl(HF:HCl:H_2O = 1:4.7:235)$, (e) $HF/HCl(HF:HCl:H_2O = 1:21.8:218)$, (f) $HF/HCl(HF:HCl:H_2O = 1:40:200)$.



Figure 3: The dependence of the remaining metallic contamination on HCl concentration at the SC-1(NH₄OH:H₂O₂:H₂O = 1:1:100) NanosprayTM 10 sec \rightarrow HF/HCl 10 sec processes; (a) initial metal contamination, (b) SC-1 \rightarrow HF(HF:H₂O = 1:240), (c) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 1:2.4:237), (d) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 1:4.7:235), (e) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 1:21.8:218), (f) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 1:40:200).

We examined the effect of HF concentration. In order to reduce oxide loss, we evaluated metal removal efficiency for SC-1 10 sec \rightarrow HCl(1:5) 10 sec. Figure 4 (b) shows the result that iron could not be removed to under the detection limit. On the other hand, iron contamination level decreased to around the detection limit at the conditions including HF in the two-step process (Figure 4 (d)). It shows clearly that slight etching by HF is necessary to remove iron. In Figure 5, we also confirmed the removal efficiency of aluminum. Figure 5(c) shows Al contamination was reduced equivalent to the blank level, which indicated our two-step process was also effective on aluminum removal.



Figure 4: The dependence of the remaining metallic contamination on HF concentration for SC-1(NH₄OH:H₂O₂:H₂O = 1:1:100) NanosprayTM 10 sec \rightarrow HF/HCl 10 sec processes; (a) initial metal contamination, (b) SC-1 \rightarrow HCl(HCl:H₂O = 1:5), (c) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 0.5:40:200), (d) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 1:40:200). LOT 12 (12)



Figure 5: The Al removal efficiency on the SC-1 (NH₄OH:H₂O₂:H₂O = 1:1:100) NanosprayTM 10 sec \rightarrow HF/HCl 10 sec processes; (a) blank; no initial contamination, (b)initial Al concentration, (c) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 1:40:200), (d) SC-1 \rightarrow HF/HCl(HF:HCl:H₂O = 0.5:40:200).

Particle Removal Efficiency

Figures 6(A, B) indicate the intermediate rinse effects on particle remaining results. In each section, the first and the second columns show initial particle counts and particle counts after the two-step process respectively. The third column is delta that is subtracted initial particle counts from after clean particle counts. At first, we investigated under no intermediate rinse condition, and the results show small increases in delta (Figure 6 (A)). It is a possible cause that a sequence of SC-1 and HF/HCl creates salt formation.

In order to prevent this salt formation, we inserted the intermediate rinse between SC-1 and HF/HCl. From various attempts, we determined the optimal intermediate rinse to be 5 sec. As shown in Figure 6 (B), it shows particle counts decreasing. The two-step process including the intermediate rinse clearly indicated the effect of preventing salt formation.

In following Figures 7, we also confirmed the particle removal efficiency concerning SC-1 concentration. Both of Si_3N_4 and PSL particles could be removed totally even in the low concentration such as the SC-1 (1:1:100) solution (Figures 7 (a)). In this study, the removal of particles is considered due to the impact power of the NanosprayTM.



Figures 6: The Effect of intermediate rinse between SC-1(NH₄OH:H₂O₂:H₂O = 1:1:100) NanosprayTM 10 sec and HF/HCl(HF:HCl:H₂O = 1:40:200) 10 sec on the particle remaining. Figure 6 (A) no intermediate rinse for 0 sec, (B) intermediate rinse for 5 sec; (a) initial particle counts, (b) particle counts after the two-step process, (c) delta; subtraction initial counts from after counts.

Electrochemical Society Proceedings Volume 2003-26



Figures 7: The Particle removal efficiency for SC-1 NanosprayTM 10 sec \rightarrow HF/HCl(HF:HCl:H₂O = 1:40:200) 10 sec on hydrophilic wafers surface. (A) Si₃N₄ particle wafer, (B) PSL particle wafer; (a) SC-1 (NH₄OH:H₂O₂:H₂O = 1:1:100) \rightarrow HF/HCl, (b) SC-1 (NH₄OH:H₂O₂:H₂O = 1:1:50) \rightarrow HF/HCl, (c) SC-1 (NH₄OH:H₂O₂:H₂O = 1:1:10) \rightarrow HF/HCl, (d) SC-1 (NH₄OH:H₂O₂:H₂O = 1:1:5) \rightarrow HF/HCl.

Etched depth, AFM images and Chemical consumption

Figure 8 shows that etched depth of thermal oxide is plotted as a function of process time. The etched depth by HF/HCl increased in proportion to process time and resulted in etching amount of 0.18 nm at HF/HCl for 10 sec. On the other hand, the etching amount of SC-1 was in no proportion to process time and almost negligible. In summary, total etched depth of our two-step process was 0.18 nm due to the effect of diluted HF. It has possibility that our two-step process achieves an etching amount of <0.1 nm below 1×10^{11} atoms/cm² of the initial metal contamination.

We also confirmed the surface roughness on the two-step process. The Ra values of a brand-new wafer before and after the two-step process were 0.097 and 0.098 nm respectively. In comparison with a brand-new wafer's AFM image, there were no increases in roughness after the two-step process due to the effects of ambient temperature and low SC-1 concentration.

Chemical consumption per a wafer was greatly improved due to a short cycle time and diluted chemicals, and reduced as below, NH_4OH (2.7 ml), H_2O_2 (2.7 ml), HF (2.1 ml) and HCl (83 ml) in a single-round condition.



CONCLUSIONS

In this study, we demonstrated an efficient single wafer wet cleaning including three main features; a short cycle time, small amount of chemical and ambient temperature. It consists of the two-step process, SC-1 (1:1:100) 10 sec with the NanosprayTM and HF/HCl (1:40:200) 10 sec. The HF/HCl played the roles of slight etching and preventing metal re-adsorption for metal removal. In addition to the effect of HF/HCl, we found the combination of SC-1 and HF/HCl to be effective on metal removal. The two-step process was also effective on particle removal as well as metal removal by applying the new two-fluid spray NanosprayTM to the first SC-1 step. In order to prevent salt formation from the combination of alkali and acid, it was necessary to insert the intermediate rinse between SC-1 and HF/HCl.

We could suppress total process time to within 90 sec due to a short cycle time on chemical processes, even if it includes out of consideration or other extra time.

Moreover, the two-step process has the features of no surface roughness and small etching amount due to diluted chemicals and ambient temperature. Total etching amount was 0.18 nm, and we are engaged in the further reduction of oxide loss.

Consequently, this two-step process is well suited to FEOL cleaning. In terms of its low chemical consumption and a short cycle time, it can be considered equivalent to the batch cleaning process.

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INNOVATIVE SURFACE PREPARATION SOLUTIONS FOR SUB-90nm IC DEVICES

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A single wafer immersion system has been shown to meet the particle, etch, and drying requirements for sub-90nm process technologies. The system is targeted for surface preparation applications including cleaning high aspect ratio devices without megasonics damage or water marks; critical cleans where ultra low Si and SiO₂ consumption is required; prediffusion cleans; and as a replacement for conventional, high concentration RCA wet cleaning processes in a batch tool. The system incorporates multiple megasonics transducers with directed beams and low power densities. It also features two drying technologies including Rapid IPA Drying and Megasonic Assisted IPA Drying which have been demonstrated to meet both watermark and defect density requirements for sub-90nm processing.

INTRODUCTION

Shorter product life cycles combined with the transition to 300mm wafer diameters are driving the semiconductor industry towards single wafer processing at all levels [1]. The potential advantages of single wafer processing for pilot lines and foundries include increased flexibility, faster time to first silicon and reduced contamination levels. The greatest challenges for single wafer wet processing systems are achieving watermark-free drying, and performing a complete cleaning process in ~ 2 minutes. This time constraint is required to approach throughputs of conventional batch wet processes, while the watermark-free drying has been a common stumbling block for most spray single wafer systems. For sub-90nm devices, single wafer processing systems can be technology enabling by minimizing film losses to maintain critical dimensions and controlling the surface state for stoichiometric film deposition. This requires achieving angstrom-level control over oxide and poly-Si consumption, as well as controlling the surface oxide regrowth during wet process sequences. We report the scope of research and results of an advanced immersion-based single wafer surface preparation system that has been shown to meet the above challenges.

Electrochemical Society Proceedings Volume 2003-26

EXPERIMENTAL

Single Wafer Process Chamber: The chamber features multiple megasonics transducers, which can be used individually, or in multiple combinations during any process or rinse step, depending upon the process application. These transducers are optimally directed in the chamber, allowing for high cleaning efficiencies at low megasonics power densities (<0.1W/cm²). A fluid distribution manifold at the chamber bottom introduces multiple chemistries, gases, or DI rinse water into the chamber. Chemistries can be introduced either in a single pass fashion or in a recirculated filtered mode for improved cost of ownership. A novel drying manifold combines an IPA vapor condensation dry with the wafer extraction from the chamber for fast, efficient drying. This two step drying process, called the Rapid IPA dry, allows for a 30 second drying sequence. A new drying technology, called megasonics-assisted drying has recently been developed as an alternative technology which offers advantages for some applications. Both drying technologies have demonstrated excellent particle and watermark performance. Experimental validation of the single wafer chamber included a variety of common Front End Of Line (FEOL) surface preparation sequences and oxide etches. Particle and watermark performance were extensively characterized, as was Si and SiO₂ consumption, oxide etch uniformity and megasonics device damage.

RESULTS

Rapid IPA Drying: Test wafers evaluated included 40:1 aspect ratio trench structures with philic/phobic interfaces, shallow trench isolation (STI) active areas, and DRAM stacked cylindrical capacitors. None of these tests, which included optical, SEM, and patterned wafer inspection analysis at customer sites, revealed the presence of any watermarks. Figure 1 shows watermark performance results on device wafers with high aspect ratio features and sub-90nm design rules, showing stiction-induced bridging that is problematic with these small geometries. This single wafer drying technology is clearly technology enabling for such wafers with high aspect ratios and extreme topography. This is especially true for HF-last processes where philic/phobic interfaces tend to trap water. HF-last surface preparation processes are becoming increasingly important for critical film depositions such as ultra-thin gate oxides, high-k gate dielectrics, DRAM storage dielectrics, and epitaxial, layers (e.g., SiGe). Achieving a short cycle time is essential for these time sensitive processes. The 30-second Rapid IPA drying meets these requirements.

Megasonic Assisted IPA Drying: A new drying method was developed to further enhance the drying capabilities of the EmersionTM single wafer chamber. In this method, the wafer is extracted out of the liquid at a relatively fast rate while IPA vapor is condensed at the wafer/gas/liquid interface as shown in Figure 2. At the same time, megasonic energy is transferred to this three-phase interface. The combined action of wafer extraction out of a liquid and the megasonics energy results in a dramatic reduction

Electrochemical Society Proceedings Volume 2003-26

in the thickness of water layer at the wafer surface which greatly reduces the amount of water to be removed during a 30 sec drying process. Figure 3 shows particle results from the Megasonic Assisted Drying process for hydrophilic 200mm wafers. The low average particle addition and tight standard deviation are a hallmark of this drying technology.

High Efficiency Megasonics Processing without Damage: As with the wafer drying step, particle cleaning processes must also be accomplished in a 30-second time frame. This is further compounded by the requirements for: 1) the use of ultra-dilute chemistries to minimize film consumption and reduce surface roughness; and 2) to avoid damage from megasonics power acting on sensitive device structures. The key factors in achieving these goals in the single wafer system is the use of ultra dilute SC-1 chemistry $(dSC-1 = 1:2:100 \text{ NH}_4\text{OH}:H_2\text{O}_2:H_2\text{O})$ in combination with the chamber's unique megasonics configuration. This megasonics configuration incorporates multiple megasonics transducers that can efficiently direct acoustic energy at the wafer surface. The combined megasonics action of the individual transducers allows for the use of low power densities (<0.5W/cm²), which avoids damage to sensitive structures. Particle removal efficiencies of >95% have been achieved routinely with aged challenge wafers using various process sequences (see Table 1). These results using a 30-second dSC1 process step demonstrate the clear benefits of using the megasonics transducers in combination to remove particles. The corresponding particle performance for a dSC1 clean on prime starting wafers is consistently neutral or particle-negative demonstrating that a 30 second process time is also sufficient to clean high quality incoming wafers. This fast acting high efficiency cleaning process is attributed to the unique megasonics configuration in the chamber.

Cleaning without Megasonics Damage: The particle removal results above show that the combined acoustic fields interact to enhance the cleaning efficacy. However, it is equally important to demonstrate that the reduced power densities used (<0.5W/cm²) can eliminate the megasonics damage that is inherent with the high power densities utilized in batch tools (>5W/cm²). Extensive testing was performed in the single wafer chamber using device structures that were known to be sensitive to megasonics damage from previous testing in batch immersion tools. The high aspect ratio stacked cylindrical capacitor structure shown in Figure 1 is highly vulnerable to lifting and collapsing in megasonics energy fields [2]. Figure 4a shows the damage that was observed in a batch immersion tool with the standard power densities that are used for particle removal. It is clearly evident that the acoustic field intensities were sufficient to damage large regions of the wafer through cavitation effects. Figure 4b shows the lack of damage noted in the single wafer chamber with a megasonics process using optimized multiple megasonic wave fronts. Patterned wafer inspection results also verified the absence of damage.

Reducing Film Loss: The high efficiency particle cleaning achieved with the use of multiple megasonics transducers enables the use of ultra dilute SC1 and very short process times, as described above. Both these factors contribute to very low film loss for oxides, metals, and poly-Si. This is especially important for controlling critical

Electrochemical Society Proceedings Volume 2003-26

dimensions (CDs) in sub-90nm structures. Table 2 summarizes film losses for typical cleaning sequences in the single wafer system.

Oxide Etch Uniformity: The single wafer system has demonstrated some of the best WIW etch uniformities ever reported, especially for thin oxide etches [3]. WIW uniformity values of $<0.5\%(1\sigma)$ have been routinely achieved for 20Å etches on 300mm wafers, as shown in Figure 5. A key point to note is that the difference between the minimum and maximum values is only 0.3Å, which is indicative of the excellent fluid dynamics in the chamber. Table 3 summarizes the WIW etch uniformities for a wide range of etch targets for thermal oxide films. Of particular note is the high temperature etching, which enables accelerated oxide etches to meet cycle time requirements for thick oxide etches, while still maintaining excellent etch uniformities.

CONCLUSION

A single wafer immersion system has been shown to meet the surface preparation challenges for sub-90nm process technologies. With unique megasonics configuration and novel drying technologies, this advanced single wafer system provides superior surface state control, damage free cleaning, watermark free drying, and ultra precision thin etch required for sub 90nm device surface preparation.

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Figure 1: SEM images of 50nm poly-Si DRAM storage cells following an HF last and dry process: (a) and (b) from non-optimized drying process showing water marks and bridging of devices; and (c) in the single wafer chamber after Rapid IPA dry, showing no watermarks.



Figure 2: Schematic showing megasonic drying process. The wafer is extracted from the rinse water with simultaneous megasonic action and IPA vapor condensation at the three-phase interface of silicon wafer/liquid and gas.



Table 1. Single Wafer Particle Removal Efficiencies with Si₃N₄ Challenge Wafers (aged >72 hours, 5k-10k pre-counts) for Different Process Sequences (sample size of ~50) With 30 sec Process Times.

PROCESS SEQUENCE	PARTICLE
	REMOVAL
	EFFICIENCY
dSC1/Rinse/Dry	95%
DIO ₃ /HF/Rinse/dSC1/Rinse/Dry	99%
dSC1/Rinse/HF/Rinse/Dry	99%

Film Material	Process	SC1Process Time	Total Film Loss(Å) per Minute	Film Uniformity
Oxide	dSC1/Rinse/Dry	440 sec	<0.1	0.46% (1σ)
Poly-Si (un- annealed)	HF/Rinse/SC1/Rinse/ Dry	1800 sec	<1	1.7% (1σ)



Figure 4: SEM images of 50nm poly-Si DRAM storage cells following a dSC1 clean with megasonics: (a) in a batch immersion tool, showing megasonic induced lifting of devices; and (b) in the single wafer chamber with multiple transducers, showing no damage.



Table 3: Oxide Etch Uniformity for Varying Etch Targets on 300mm Wafers.

Figure 5: Oxide etch uniformity for (a) a 20Å etch on a 300mm wafer showing a WIW uniformity (0.4%, 1 σ) and a maximum difference across the wafer of only 0.3Å; and (b) a 10Å etch on a 200mm wafer showing a WIW uniformity (0.96%, 1 σ) and a maximum difference across the wafer of only 0.45Å.

PREDICTIVE MODEL-BASED CONTROL OF CRITICAL OXIDE ETCHES FOR SUB-100NM PROCESSES IN A SINGLE WAFER WET PROCESSING SYSTEM

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The etching kinetics of thermally grown SiO_2 were investigated in dilute HF solutions (100:1 to 500:1) as a function of temperature, HF concentration, and fluid dynamics. Results from this study support a model with surface chemical reaction-controlled kinetics with an activation energy of about 32 kJ/mole. As expected, the oxide etch rate strongly depends upon HF concentration. The etching mechanism is briefly discussed with regard to species distribution considerations. Based on these experimental results, a predictive model has been developed for critical oxide etch process control. The model takes etch target as the sole operator input and automatically determines the required etch time, depending upon real-time process conditions. These conditions include HF temperature, HF concentration, and the number of wafers that have been processed through the system. Results using this model based control show excellent WIW and WTW etch uniformity for thin oxide etch process in a single wafer immersion processing system.

INTRODUCTION

 SiO_2 etch plays a very important role in many processes steps in today's device manufacturing such as patterning windows and surface passivation. The preferred method for SiO_2 etch is a wet etch process based on HF chemistry. It is generally agreed that the overall thermodynamic reaction involved in the wet etch process is as the following (1-3):

$$SiO_2 + 6HF = 2H^+ + SiF_6^{-2} + H_2O$$

It is well observed that this reaction is isotropic for amorphous SiO_2 but anisotropic for quartz (1, 4). Although there is a general agreement on thermodynamic aspects of SiO_2 dissolution, understanding of etch kinetics and mechanisms remain limited and in some cases even contradictory (1-6). For example, Tso et al. have found in their research that the reaction of SiO_2 with HF solution is mass transfer controlled (5). While other researchers have found that the dissolution rate of fused SiO_2 was independent of agitation intensity and concluded that the reaction rate is surface chemical reaction controlled (1). More recently, studies on SiO_2 etching in silicon IC industry have been reported (4,6). However, models developed were complicated so that application of such

Electrochemical Society Proceedings Volume 2003-26

models in device making process was rather difficult. In this current study, thermally grown SiO₂ etch rate in diluted HF solution (0.5 M to 0.05 M, 50:1 to 500:1) was investigated. The objective of this study was to develop a simple etch model that could be effectively used for process control in SiO₂ critical etch applications.

EXPERIMENTAL

200 mm silicon wafers with 500 Å dry thermally grown silicon dioxide were used in this study. The uniformity of the oxide layer on these wafers was <1% at 1 σ . Etching was performed using a mixture of DI H₂O and HF. The HF chemical used was semiconductor grade commercial product with 49% w/w concentration (Morita Chemical Osaka, Japan). Ultra high purity de-ionized water (> 18M Ω -cm) was used to dilute the HF to desired concentrations. An SCP Global Technolgies' single wafer tool, the EmersionTM 200, was used to etch the wafers. Oxide layer thickness was measured immediately before and after the etch experiment to determine the etch removal and etch rate using a high resolution M88 ellipsometer (JA Woolam, Nebraska, USA). A total of 49 points were measured on each wafer surface. During etching, the process temperature was maintained with a solid state control system (SSCS) within 0.1 °C. of the temperature set point. HF concentration was measured using a conductivity probe. It was found that the HF concentration determined from conductivity probe agreed with those determined from NaOH titration within 1% error.

RESULTS AND DISCUSSION

Effect of Fluid Dynamics

For SiO₂ dissolution in HF, both reaction controlled and mass transfer controlled kinetics have been proposed (1,5). A simple way to determine whether mass transfer is the rate controlling step is to vary the liquid velocity relative to the solid because velocity determines the diffusion boundary layer thickness and therefore the mass transfer rate. If a reaction is mass transfer controlled, the rate will have a clear dependency on the fluid dynamics i.e. the HF flow rate used during the etch process. On the other hand, if etch rate is controlled by chemical reaction, there is no such dependency for well mixed systems. SiO₂ etch rate was studied as a function of HF flow rate in this work. Figure 1 shows that oxide etch rate is essentially independent of HF flow rate changes. This is a clear indication of chemical reaction controlled kinetics. These results agree with the conclusions of many other researchers (1, 7).

Effect of Temperature on Etch Rate

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The effect of temperature on the SiO_2 etch rate is shown in Figure 2 for two different HF concentrations. It can be seen from Figure 2 that the slopes of curves for different HF

concentration are approximately the same. An activation energy of 32 KJ/mole (7.6 Kcal/mole) is calculated from this data. This value agrees reasonably well with the data reported in literature (1,5). This activation energy is also in accordance with a reaction controlled kinetics.



Figure 1. Effect of HF flowrate on SiO_2 etch rate and etch uniformity



Figure 2. Effect of temperature on SiO_2 etch rate

Effect of HF Concentration on Etch Rate

SiO₂ etch rate as a function of HF concentration at 22 °C is shown in Figure 3. As can be seen from Figure 3, the etch rate has a linear relationship with the total fluoride concentration in the range from about 0.05 M to about 0.6 M (500:1 to 50:1 v/v). These results agree very well with what has been reported in the literature for dilute HF concentration range (2,5).

A first order etch model was developed based on these results. It is expressed as:

$$R=K[C_F] - A \quad (1)$$

Where $[C_F]$ is the total fluoride concentration, K and A are constants. At 22 °C, K=96.5 Å/minute and A= 3.42 Å/minute. It is interesting to note that the rate falls to zero before $[C_F]$ goes to zero. A similar linear model with a non-zero intercept was also reported by Judge et al (3). This non-zero constant may arise for several reasons. First, it could be due to system error in measuring HF concentration or system error from the determination of the oxide layer thickness using the ellipsometer. Second, it may be due to change in effective etch species and/or etch mechanism as many authors have suggested (2,4,6). Finally, HF dissociates significantly in dilute solution to H⁺ and F⁻, and F⁻ is not effective for SiO₂ etching (2,4,6). When the total fluoride concentration is used in Equation (1), the effective species are over represented by the total fluoride concentration. Therefore, a negative intercept results. However, detailed analysis showed

that this dissociation issue only contributed about 11% of the negative constant associated with the model at 22 °C. Further tests are required to sort out the reason for this negative intercept.

Solution Equilibrium and Etch Mechanism

In diluted HF solutions, following equilibria exist:

HF = H= + F-	(2)	$K_1 = [H+][F^-]/[HF]$
$HF+F^{-}=HF_{2}^{-}$	(3)	$K_2 = [HF_2^-]/[HF][F^-]$
$2HF = H_2F_2$	(4)	$K_3 = [H_2F_2]/[HF]^2$

The respective equilibrium constants $K_1 = 6.85 \times 10^{-4}$ mole/liter, $K_2 = 3.963$ liter/mole, and $K_3 = 2.7$ liter/mole are frequently cited (2,4). Also, the charge and mass must be balanced in the solution resulting in:

$$[H=] = [F-] + [HF2-]$$
(5)
$$[C_F] = [HF] + [H2F2] + [F-] + [HF2-]$$
(6)

Solving equations (2) through (6), the species distribution is obtained. Figure 4 shows the distributions of the species' mole fraction relative to the total fluorite concentration $[C_F]$. As can be seen in Figure 4, the dominant species in the dilute HF concentration range of interest in this work are HF and the H_2F_2 dimer. At very low concentration (< 0.1 M), HF dissociation starts becoming significant along with HF and H_2F_2 . However, the most dominant species is HF. Finally, the HF₂ species concentration is more than an order of magnitude lower than that of either HF and H_2F_2 . It increases with the total concentration increases from 0 to 0.1 quickly and reaches a plateau at about 0.1 M.

Figure 5 shows a different representation of the species distribution in diluted HF solution without any pH adjustment. A linear model does not represent any of these species' concentration profiles very well as shown in Figure 5. Furthermore, because all these species are interrelated, it is impossible to determine the etch mechanism by fitting the etch data to any particular species. For example, if the rate is modeled as:

$$\mathbf{R} = \mathbf{K}[\mathbf{H}_2\mathbf{F}_2],$$

from equation (4), $[H_2F_2]=K3[HF]^2$,

$$R=K[H_2F_2]=KK3[HF]^2$$
(7)

The etch data from this study shows that there are no significant etch rate differences between those fluoride species. The reason is that the etch rate is linear with the total fluoride concentration. Considering all the active species in the solution the etch rate can be expressed as:

$R = C1[HF] + C2[H_2F_2] + C3[HF_2] + C4[F] - C5$ (8)

Where C1 through C5 are constants. As the total concentration changes from 0.1 M to 0.5 M, the relative concentration of the species change significantly as shown in Figure 4. However, the etch rate holds the linear relationship very well in this concentration range. The only explanation for this is that all the species have a similar etch rate. A possible explanation is that the H_2F_2 dimers are linked together by weak hydrogen bond. The hydrogen bond does not need high energy to break up. It has been reported that the H_2F_2 dimers break up at radiation energy of at a frequency of 1000 cm⁻¹ (8). This break up energy is equivalent to about 11.96 kJ/mole. It has been determined from this research that the activation energy for the etch reaction is 32kJ/mole. Therefore, dimers actually break down to monomers when it obtains the required energy to react with the SiO₂. From the above analysis, it seems reasonable to believe HF is the dominant etch species in dilute HF solution.



Figure 3. SiO_2 etch rate as a function of total fluoride concentration at $22^{\circ}C$

Figure 4. Calculated species mole fraction as a function of total fluoride concentration

Practical Application of the Etch Model

As the device manufacturing is advancing to the sub-100 nm technology nodes, one of the primary challenges facing the traditional wet cleaning/etch process is the precise etching of oxide films to the Angstrom level. In this regard, SCP Global Technologies has developed a single wafer wet processing system (EmersionTM) based on immersion principles unlike the traditional single wafer spin process systems. Improved fluid

dynamics and faster quenching features enable the EmersionTM process chamber to yield excellent within wafer (WIW) etch uniformity performance (<0.5% @ 1 σ for 20 Å removal) as shown in Figure 7. However, controlling wafer to wafer (WTW) uniformity in single wafer systems is much more challenging because it requires that each wafer sees identical process conditions. Based on the understanding of the etch mechanism and the model discussed in the previous sections, a control algorithm has been developed in order to address the WTW uniformity challeges. This control algorithm takes the etch target as the sole operator input and provides the etch time as an output based bath life, HF concentration, and temperature of the HF solution. A 500 wafer marathon run has been conducted with a 20 A target SiO₂ etch. These results are shown in Figure 6. It can be seen that WTW uniformity or run to run repeatability is 0.4% at 1 σ . Both WIW and WTW uniformity levels demonstrated in this work are among the best reported for any wet processing system.

SUMMARY

The rate of SiO₂ etch by HF is strongly dependent upon the HF concentration and temperature. The experimental data in this investigation support a chemical reaction controlled rate with an activation energy of about 32kJ/mole. Experimental data and solution chemistry analysis suggested that the dominant active species is HF. H_2F_2 dimers actually break down to monomers when they have the energy to react with SiO₂ molecules. Finally, a control algorithm based on etch rate model has been developed for the SCP Emersion single wafer tool. Industry leading WTW and WIW uniformities have been achieved using the etch control algorithm.



Figure 5.Calculated species concentration as a function of total fluoride concentration.

Figure 6. WTW SiO2 etch uniformity achieved with the predictive model control algorithm.





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NON-IPA WAFER DRYING TECHNOLOGY FOR SINGLE-SPIN WET CLEANING

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ABSTRACT

We investigated the relationship between the dissolved silicon from wafer surface treated with HF and oxygen concentration, and confirmed that the higher oxygen concentration resulted in increased dissolved silicon concentration in accordance with the mechanism of water mark formation. We established a non-IPA wafer drying technology, which can control oxygen concentration near wafer surface during not only dry steps but also rinse steps. By using the equipment into which this drying system was introduced, we evaluated water marks on wafer surface when the oxygen concentration near wafer surface during the rinse and the dry step were varied. As a result, no water marks were found only in the condition oxygen concentration near wafer surface was controlled during both rinse and dry steps. Therefore, we confirmed that it is important to control the oxygen concentration near wafer surface at not only dry steps but also rinse steps in order to prevent water marks.

INTRODUCTION

Wafer drying is one of the most important steps in the wet cleaning process. Recently, wet cleaning process has been changing over from batch to single cleaning(1). For a single-spin wet cleaning, spin-drying is the most common wafer drying technique. However, conventional spin-drying tends to leave water marks on wafer surface more easily than IPA-drying. Therefore wafer drying has been one of the technical issues for a single-spin wet cleaning equipment and it is indispensable to develop water mark free drying technique. On the other hand, it has been reported that there is a possibility that IPA could remain on wafer surface after IPA-drying and these residue would form Si-C bonds during heat treatment, which might degrade thin oxide reliability (2).

The mechanism of water mark formation after a HF process is considered as follows(3).

1) Oxygen dissolves into a water drop and diffuses to silicon surface.

2) Dissolved oxygen oxidizes silicon surface and the silica dissolves into water.

3) After the water drop is dried, the silica remains on wafer surface. This residue of dissolved silica is considered water marks. In this mechanism, it is considered that dissolved oxygen causes water marks formation and water marks consist of dissolved silica.

Electrochemical Society Proceedings Volume 2003-26

In this study, based on this mechanism, we investigated the dependence of the dissolved silicon from wafer surface treated with HF on the oxygen concentration. And we established a new non-IPA wafer drying technology which was aimed at applying for single-spin wet cleaning. This new drying technology can control oxygen concentration near wafer surface during rinse and dry steps. By using the equipment into which this new drying system was introduced, we also evaluated water marks on wafer surface in comparison with the result of the dissolved silicon evaluation.

EXPERIMENTAL

Experiment about Dissolved Silicon

In this experiment, 200mm in diameter n^+ polycrystalline silicon wafer (P-doped 4E20atoms/cm3) was used.

Fig.1 shows the procedure for this experiment.

- 1. The oxygen concentration in the box was controlled by supplying nitrogen into the box. The polycrystalline silicon wafer was treated for 2min with 1wt% HF solution. The hydrophobic wafer was transferred into the box immediately.
- 2.De-ionized water(100cc) was supplied onto wafer surface, then the water covered the hydrophobic wafer surface. After the fixed time passed, we collected the DIW.
- 3.The silicon concentration in DIW was measured by flame-less atomic absorption spectrophotometer(FL-AAS Varian Spectr AA880Z)

Water Mark Evaluations

MP-2000, single-spin wet cleaning equipment, was used for this evaluation. The equipment is installed with the drying technology which controls oxygen concentration near wafer surface during rinse and dry steps. Fig. 2 shows the schematic view of our proposal drying system. Nitrogen and DIW are supplied onto wafer from the center of the shield-plate and the spin-base. A wafer is hold by a chuck set in the spin-base. The shield-plate and the spin-base rotate simultaneously, and the shield-plate also moves up and down. This equipment controls the oxygen concentration near wafer surface during rinse and dry steps and shortens the drying time by supplying nitrogen from the center of shield-plate and controlling the distance between the shield-plate and the wafer.

In this evaluation, 200mm in diameter n^+ polycrystalline silicon wafer with pattern (P-doped 4E20atoms/cm3) were used. The patterned wafer has lines and spaces of various widths (0.25-20• m), and the height of pattern is 500nm. We evaluated water marks which had formed on the wafer surface after a HF etching process. The number and the size of the water marks were counted by KLA-2132.

RESULT AND DISCUSSION

In the evaluation of dissolved silicon, we investigated the dependence of the amount of dissolved silicon from wafer surface on the oxygen concentration. The results are shown

Electrochemical Society Proceedings Volume 2003-26

in Figs. 3 and 4. Fig. 3 shows the dependence on dissolved oxygen concentration. The higher dissolved oxygen concentration resulted in increased dissolved silicon concentration. And as the dissolving time becomes longer, the amount of dissolved silicon increased. Fig. 4 shows the dependence on ambient oxygen concentration. Also in this result, the higher ambient oxygen concentration resulted in increased amount of dissolved silicon. These results indicate that dissolved oxygen and ambient oxygen causes dissolved silicon in accordance with the mechanism of water mark formation. Therefore we realized that it is important to reduce dissolved oxygen concentration and ambient oxygen concentration in order to prevent water marks.

We also measured the change of dissolved oxygen concentration. In this measurement, we changed the ambient oxygen concentration and the condition water was agitated or not. The data is shown in Fig. 5. When the ambient oxygen concentration was controlled, dissolved oxygen concentration didn't increase. And oxygen did not dissolve into water so quickly when the water was static under ambient air. However, in the condition that the water was agitated under ambient air, oxygen dissolved into water quickly. In a real single-spin process, DIW rinse flows on wafer surface from the center to the edge with swirling. Therefore, this data clearly indicates that oxygen concentration in rinse water increases instantly during the rinse step under ambient air. From this result, we also confirmed that it is important to control oxygen concentration even during the rinse step in order to suppress dissolved oxygen concentration

The oxygen concentration between shield-plate and wafer was measured in the condition that shield-plate gap was 5mm, nitrogen flow rate was 100LM, and the wafer size was 300mm in diameter. The result is shown in Fig. 6. The concentration was measured at two points, one was 50mm from the center, and the other was 145mm. Immediately after nitrogen supply started, the oxygen concentration at both positions decreased rapidly. This equipment can perform most of the rinse step in the condition the shield-plate is close to wafer. This data clearly indicate that this equipment can controls oxygen concentration during rinse and dry steps, and the oxygen concentration decrease to under 40ppm over entire wafer surface by the time spin-drying starts.

We evaluated water marks which was formed on patterned polycrystalline silicon after the HF etching process. In this evaluation, the oxygen concentration near wafer surface during rinse and dry steps were varied. Fig. 7 shows the test condition and the result. In the first condition, the distance between shield-plate and wafer was fixed at 150mm during both rinse and dry steps. In this case, the oxygen concentration near wafer surface was approximately 20% from the rinse step through the dry step. In the second condition, the shield-plate gap was 150mm at the rinse step and then narrowed to 2mm at the dry step. In this case, the oxygen concentration near wafer surface was approximately 20% at the rinse step, however it decreased after the dry step started. In the third condition, the shield-plate gap was 5mm at the rinse step and then narrowed to 2mm at the dry step. In this case, oxygen concentration near wafer surface decreased after the rinse step started, and at the time the dry step started it decreased down to under 40ppm over entire wafer surface .Right side graph shows these results. The horizontal axis shows the water mark area which was calculated from the number and the size of water marks.

In the first condition, a large number of water marks were found and their size was very big. In the second condition, we still find a large number of water marks. In the third condition, there are no water marks on wafer surface.

The result of water mark evaluation corresponds with the results of dissolved silicon evaluation and the result of dissolved oxygen concentration measurement. We consider that the difference between the results obtained in the first condition and the second condition was caused by the difference in dissolved oxygen concentration and the difference in drying time, and the difference between the result of the second condition and the third condition was due to the difference in dissolved oxygen concentration. From these results, we confirmed that it is important to control oxygen concentration during not only dry steps but also rinse steps in order to prevent water marks.

CONCLUSIONS

From the result of the evaluation about dissolved silicon, we confirmed that the higher dissolved oxygen concentration resulted in increased dissolved silicon concentration in accordance with the mechanism of water mark formation. And we also confirmed that oxygen dissolved into water rapidly at rinse steps under ambient air. Based on these experimental findings, we established a non-IPA wafer drying technology, which can control oxygen concentration near wafer surface during rinse and dry steps.

In the water mark evaluation using this equipment, we succeeded in preventing water marks completely by controlling oxygen concentration near wafer surface at not only the dry step but also the rinse step.

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FIGURES



Fig. 1 The procedure for dissolved silicon experiment.









61



Fig. 4 The dependence of dissolved silicon on the ambient oxygen concentration



Fig. 5 The dependence of dissolved oxygen concentration on ambient oxygen concentration and agitation. (a) The dissolved oxygen concentration under Nitrogen(ambient O2 concentration is 6ppm) with agitation, (b) The dissolved oxygen concentration under ambient air and with agitation, (c) The dissolved oxygen concentration under ambient air and without agitation(water is static)



Fig. 6 The oxygen concentration between shield-palate and wafer.



Fig. 7 The test condition and result of water mark evaluation.

(a) both rinse and dry step were done under ambient air, (b) rinse step was done under air and dry step was done in the condition oxygen concentration was controlled, (c) both rinse and dry step were done in the condition oxygen concentration was controlled.

Electrochemical Society Proceedings Volume 2003-26

Front End of the Line Cleaning

INTEGRATION OF HIGH-K GATE DIELECTRICS – WET ETCH, CLEANING AND SURFACE CONDITIONING

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For decades, IC manufacturing has been relying on Si-based materials – especially for the critical front-end-of-line processes. Driven by scaling requirements, the gate dielectric will have to be replaced by materials with a higher dielectric constant. These 'metaloxide' materials pose certain concerns on contamination control. Further, interface preparation (or cleaning) of the silicon substrates prior to high-k deposition is an emerging field, as the quality of the deposited layer and the scaling potential critically depend on these steps. Finally, also the selective removal of these materials after gate stack patterning is considered.

INTRODUCTION

New dielectrics with higher dielectric constant, referred to as "high-k materials", are expected to replace the silicon oxide as gate dielectric in future electronic devices. Several candidate materials and deposition processes are currently under investigation, however it appears there is consensus with (Zr or) Hf based materials. Although excellent equivalent oxide thickness (EOT) and leakage scaling performance has been demonstrated, also with these materials, several possible performance and integration issues have been identified. In this paper, we will focus on issues related to wet processing aspects associated with high-k dielectric gate stack integration. Focus will be on contamination control, including cleaning and metrology, on surface conditioning prior to high-k deposition and on selective wet etch of high-k dielectrics, respectively.

EXPERIMENTAL

 HfO_2 films are deposited on p- and n-type silicon device wafers (200mm, Cz, <100>) using commercially available chemical vapor deposition (CVD) tools. Typically, prior to high-k deposition, wet or plasma based surface conditioning is done to achieve enhanced growth. Prior to gate electrode deposition, the stacks received a post deposition anneal (PDA) treatment in O₂ or N₂, at temperatures between 500 and 800°C. Unless otherwise mentioned, wafers were processed using a furnace LPCVD poly process at 550°C using

Electrochemical Society Proceedings Volume 2003-26

 SiH_4 (no carrier gas). Conventional cleaning sequences (i.e. HF, SC-1, SC-2 or O3/DI based) have been used for cleaning, surface conditioning and contamination control.

TXRF analysis was performed with a FEI-ATOMIKA 8300 W system equipped with a W or Mo tube operated at 50 kV and 55 mA. Different filters were used in the different excitation modes (WL β and WL α : no filter, MoK α : Zr filter, MoK β : Rh filter). The tool is equipped with a tunable multilayer. All measurements were done at 70% of the critical angle, for 1000 sec live time. Calibration is performed with a 1 ng Ni micro droplet type Si wafer standard (FEI-ATOMIKA).

RESULTS AND DISCUSSION

Contamination control

The introduction of new materials has implications for standard processing. One has to deal with cross contamination risks of Hf and Zr on Si wafers, as these materials could result in yield losses in the standard processing. Contamination monitoring strategies for these new elements must be developed. All these steps require an appropriate analysis methodology for Zr and Hf trace contaminant detection on Si wafers. Total Reflection X-Ray Fluorescence Spectroscopy (TXRF) is a well-established technique for metallic trace analysis on Si wafers. The technique offers a multi-element analysis capability with Detection Limits (DL) in the order of E10-E11 at/cm² for most elements [1]. The combination with the preconcentration method Vapor Phase Decomposition – Droplet Collection allows DL of E8-E9 at/cm² [2] [3]. Further, the application of TXRF could also be considered for contaminant analysis in thin high-k dielectric films. For both applications, a careful selection of the excitation energy is required to obtain ideal DL – either for Hf or Zr trace contaminant analysis on Si substrates, or for general trace contaminant analysis in HfO₂ or ZrO₂ dielectric films.

An overview of the various TXRF excitation modes and corresponding excitation energy is given in Table 1. In addition, this table contains the main excitation line of either Zr or Hf. The TXRF analysis of Hf is rather straightforward using the conventional excitation modes WL β and MoK α excellent detection limits can be achieved. The sensitivity should be highest for the WL β excitation energy (9.67 keV) as the energy is closer to the absorption edge for HfL (9.56 keV) compared to the MoKa energy (17.44 keV). In case of the MoK α excitation however, the HfL peak appears in a low background energy region compared to the case of WL β excitation. As such, similar DL of about 1E10 at/cm² is obtained for both excitation modes. For Zr detection however, traditional excitation modes WL β and MoK β are unable to excite the Zr line. In the WL β excitation mode only the Zr L line (not shown) can be excited and this with low efficiency. The low sensitivity and high background result in bad DL of about 3E12 at/cm² (Table 1). The MoK α excitation mode suffers from the same limitations – the excitation energy of MoK α (17.44 keV) is not sufficiently high to excite the Zr K line. However, despite the Zr filters in the X-ray path and because of the rather high bandwidth of multilayer monochromators, in practice some excitation is possible (DL \sim 3E12 at/cm²). Better sensitivity can be achieved with a MoK β (19.63 keV) excitation mode (excitation energy above the absorption edge for the Zr K line). This results in an adequate DL of about 3E10 at/cm².

		Zr	Hf
Excitation	Energy	Zr K line (~18 keV)	HfLline (~9-11keV)
WLα	8.40 keV	not.det.	not.det.
WLβ	9.67 keV	not.det.	1.2E10 at/cm ²
ΜοΚα	17.44 keV	poor (3E12 at/cm ²) 8.1E9 at/cm ²	
ΜοΚβ	19.63 keV	2.5E10 at/cm ²	3.0E10 at/cm ²

Table 1: Overview of the different (routine) TXRF excitation modes and the corresponding sensitivity for Zr or Hf contaminant analysis.

The situation is completely different when one wants to realize adequate DL for traces in/on a high-k layer since efficient excitation of the core elements needs to be avoided. A high excitation efficiency for the substrate elements would lead to detector saturation and in addition can lead to peak interference with contaminant elements of interest.

For HfO₂ films excitation with WL β (9.67 keV), MoK α (17.44 keV) or MoK β (19.63 keV) causes excitation of the L absorption lines (LI 11.271, LII 10.739 and LIII 9.561 keV). The Hf L lines are intensively present in the spectrum (Figure 1a). Unfortunately, this region also contains the peak positions of many interesting contaminants as Fe, Co, Ni, Cu and Zn. Indeed, the advantages for Hf detection on Si wafers turn into a disadvantage for the detection of traces in HfO₂ films. The use of WL α excitation energy (8.40 keV) is suitable for layer analysis as no excitation of the Hf lines occurs (Table 1). The whole energy range from 2 to 8 keV is interference and background free. The analysis of S to Ni is hence possible. As an example, a Ti level of 3.8E11 at/cm² could be detected using WL α , whereas the result from an analysis in the WL β mode was <1E12 at/cm² for the same sample (Figure 3).

It is clearly demonstrated that TXRF - by control of the excitation mode - is a viable technology for contaminant analysis on silicon substrates and in (thin) high-k dielectric films. The application of preconcentration procedures allows further sensitivity enhancement for contaminant analysis of Si substrates [4].



Figure 1: TXRF spectrum of a 10 cycles ALCVDHfO₂ film (1 nm) with (a) WL β excitation, 2.3 mrad, 1000 sec, Zr filter (b) WL α excitation, 2.6 mrad, 1000 sec, no filter

Electrochemical Society Proceedings Volume 2003-26

Cleaning of high-k materials

The introduction of new materials is typically accompanied by a concern on the impact of these materials on conventional processes. A specific concern exists with the behavior of high-k materials in a cleaning bath. Once high-k material is introduced into a wet processing tank (e.g. after an etch step), it is obvious that re-deposition might occur. To examine this metal (re-)deposition, typical cleaning mixtures were deliberately contaminated at a level ranging from 0.1 up to 10 ppm. These are realistic values, because the dissolution of 2 nm of HfO_2 for 50 wafers in a bath with a volume of 20 l, yields a bath loading of 1 ppm. The effects of either a contaminated rinse or a contaminated clean (followed by a non-contaminated rinse) were investigated separately. Figure 2A shows the scheme for a contaminated rinse with on the one hand a dilute HCl rinse (pH 2) either followed by an acidic(I) or a neutral(II) drying step and on the other hand, an all-neutral rinse/dry step (III). Figure 2B shows the scheme for a contaminated clean with on the one hand a dilute APM clean (vol. ratio 1/1/48, pH 10.5) either followed by an all-acid(IV) or an all-neutral(V) rinse/dry step, and on the other hand a concentrated APM (1/1/5, pH 10.2) followed by an all-neutral rinse/dry step (VI). Identical tests (scheme B) have been performed with 0.5% HF solutions.







Figure 3: Re-deposition of dissolved Hf and Zr from (a) dHCl/2 (I) \boxtimes , dHCl/7 (II) \boxtimes , and DI/7 (III) \equiv , and from (b) dAPM/2 (IV) \boxtimes , dAPM/7 (V) \boxtimes , and APM/7 (VI) \equiv . /2 or /7 indicates the pH during (a) drying or (b) rinse + drying.

Figure 3a shows that for the contaminated rinse, the largest deposition is observed for the all-neutral(III) case. For the all-acid(I) case the resulting contamination is almost one order of magnitude lower. When an acid rinse is used in combination with a neutral drying step (II), wafer surface contamination is between both previous extremes. Considering the pH at boundary layer level, it is clear that for condition I the pH remains at 2, and for condition III the pH remains neutral. For condition II, the pH of the boundary layer rises during the rinse step, approaching neutrality. The data suggest that a higher pH-value in the boundary layer results in an increased deposition. Figure 3b shows that for the contaminated APM-clean, an acid rinse results in a higher final surface

contamination than a neutral rinse. Again considering the pH in the boundary layer, it is clear that an acid rinse (IV) reduces the pH to a lower level than a neutral rinse (V&VI). The data suggest that a neutral pH in the boundary layer increases the deposition. These results can be explained by the fact that the solubility of the hydrous oxides of these high-k materials shows a minimum around pH 7 [5] [6]. In the case of HF-cleaning no surface contamination has been observed – indicating that HF based chemistries are ideal cleaning mixtures for high-k material.

Surface conditioning before high-k deposition

Contrary to conventional gate dielectrics (SiO₂ based), which are achieved by thermal oxidation of the silicon substrates, the new generation high-k dielectrics are achieved by chemical deposition processes. It has been elaborately demonstrated that these chemical deposition processes in general and atomic layer deposition (ALD) in particular are extremely dependent on the interface quality prior to gate dielectric deposition [7]. In Figure 4a ALD growth curves (i.e. Hf coverage determined by Rutherford Backscattering Spectroscopy versus number of ALD cycles) are presented as a function of the interface pre-treatment. A clear dependence in growth rate (deviation from linear growth) is observed for HF last interfaces, while passivating chemical oxide layers (with OH termination) result in close to linear dependencies. Yet, as can be seen from Figure 4b, a completely passivating chemical oxide has a physical thickness of about 1.0nm and as such contributes predominantly to the overall EOT of the gate stack. Moreover with these physical thicknesses, sub 1.0nm EOT scaling is virtually impossible. Therefore, ideally the interface preparation process should yield close to a monolayer chemical oxide, without any backbond oxidation to occur. The growth of passivating interfacial oxide layers by ozonated chemistries has been studied elaborately in the past [8], see also Figure 5. It was observed that the interfacial oxide thickness is dependent on oxidation time and ozone concentration. By modulating an ozone based clean, i.e. by saturating the cleaning bath to an ozone concentration of 1ppm respectively 3ppm, and controlling the immersion time, uniform oxide thickness of 0.4nm and 0.7nm (based on ellipsometry) could be achieved. More details on the ozone process can be found elsewhere [9].



Figure 4: A crucial equilibrium (a) ALD based growth curves and its dependency on interface preparation and (b) the EOT impact of interfacial SiO₂.

Electrochemical Society Proceedings Volume 2003-26



Figure 5: Interfacial oxide deposition dependency on [O3] and time [8].

f = 10 kHz, 50x50 µm²

EOT= 0.91 nm

0.7 nm

Lot#: HK02116 Wafer#: D10, 15

IMEC clean

EOT= 1.1 nm

PVD TiN Gate

-2

2.5nm ALCVD HfO

80

60

40

20

0

Capacitance (pF)

72



Figure 6: Achieving 0.7nm and 0.4nm thick interfacial SiO₂ layers with O₃ clean.



0.8

deposited on IMEC clean (1.0nm) and 0.7nm chemical oxide.

-1

Gate Voltage (V)

Figure 7: CV curves for HfO₂ layer Figure 8: Cumulative leakage distribution for HfO₂ laver deposited on ozone based interfaces (Figure 7).

The performance and benefit of these scaled chemical oxides can be clearly seen from the CV and cumulative gate leakage curves shown in Figure 7 and Figure 8. From the CV curves shown in Figure 8, it can be clearly seen that 2.5nm HfO_2 on either an IMEC clean interface (1.0nm SiO₂ interface) yields a higher EOT than a comparable high-k layer on a scaled 0.7nm EOT ozone interface. The net gain is of the order of 0.3nm, as anticipated. Figure 8 clearly indicates the decent uniformity achieved for the 0.7nm interface layer process, compared to a passivating IMEC clean treatment. Virtually no difference is observed between both layers, other than the higher leakage (lower EOT) for the 0.7nm based process. This clearly indicates the value of interface scaling. However care has to be taken, not only to prepare these interfaces, but also during further processing of these layers as can be seen in Figure 9. For this Figure, a 0.4nm and 0.7nm interfacial oxide were analyzed by means of XPS, after interface oxidation, after high-k deposition and after anneal treatment. It can be seen that after interface oxidation, both processes are distinctly different in thickness. However, after high-k deposition, the effect becomes marginal, indicating the critical equilibrium of the interface pretreatment. Further, after thermal anneal treatment, both interface layers increase in thickness. Despite this, with proper control of the overall transistor process, excellent EOT scaled

devices can be manufactured as seen in Figure 10. EOT scaling down to 0.7nm EOT was achieved. More details on these EOT scaled devices was presented elsewhere [10].



by further processing.



Figure 9: Growth of interfacial oxide layer Figure 10: Jg versus EOT for HfO_2 on scaled chemical oxides demonstrating sub 1.0nm EOT.

Selective etching of high-k materials

Successful integration of high-k gate stacks also requires attention to the optimization of the gate patterning. More specifically, a selective removal of high-k films over the source/drain area, is desired (i.e. with minimal recess). A complete dry process is either sputter based and results in poor selectivity towards the silicon substrate or is chemical based resulting in excess polymer formation leading to high-k footing [11]. This section reports on the development and optimization of a selective wet chemical solution for removal of CVD HfO₂-based films. A wet removal alone is not feasible when the high-k material is thermally treated, which is mostly the case in devices. The thermal treatment makes the high-k layer resistant to standard wet chemistries [12], and therefore difficult to remove selectively. The 1:3 selectivity obtained for as-deposited HfO_2 towards thermal oxide, drastically decreases to 1:30 after annealing HfO₂ layers (Figure 11).

A way to enhance wet chemical etching of annealed (crystalline) high-k layers is by means of damaging the layer prior to exposure to a selective etch chemistry. In this work, the damage of CVD HfO₂-based layers is achieved either by ions present in a high-k etch plasma process or by ion implantation at low energies. It has long been known that ion implantation damage can increase wet etch rates of SiO_2 films [13]. However, in the case of thin high-k layers, low energy ion bombardment is preferred to the high ion energies typically used for implantation of SiO_2 . This is to avoid unacceptable substrate damage. The effectiveness of ion implantation as a means of altering the crystalline structure of HfO₂ to enhance wet chemical etching either by a physical damage or a chemical mechanism was shown before [14]. Also, high-k layer damage by ion bombardment supplied by an oxygen plasma in a reactive ion etching tool was reported [15] (see also Figure 12).





Figure 11: Etch rates of CVD HfO_2 for (a) as-deposited and annealed (PDA) compared with thermal oxide (Thox)

Figure 12: Etch rate of thermal treated ALD HfO_2 after implantation with "neutral" ions when etched with etchant 1 (HF based).

However, the main constraint is not the etch rate but the poor selectivity towards SiO_2 layers. Once damaged, the high-k layer must be removed selectively towards all layers (oxides, silicon and Si_3N_4 layers) present at that time during processing. From literature, it is known that mostly HF is used to etch HfO₂-based films and that the etch rate increases with the concentration of HF used [16]. Without optimization of these HF-based etch solutions, only limited selectivity to the exposed can be achieved.

We have developed a chemistry that achieves higher selectivity (than HF) towards SiO_2 , providing at the same time a reasonable HfO_2 etch rate. The selective etch mixture consists of three components, i.e. an alcohol, HF and an acid, each of them playing a specific role in the etching mechanism. The HF component in the etch mixture is of great importance since it provides the active species for HfO_2 removal. It is also well known that in dilute HF (< 1M), the following equilibriums are established:

$$HF \Leftrightarrow H^+ + F^- \tag{1}$$

$$HF + F^{-} \Leftrightarrow HF_{2}^{-}$$
 [2]

$$2HF \Leftrightarrow H_2F_2$$
 [3]

By varying the solution composition, one can select an etching mechanism by HF_2 , H_2F_2 or a combination of both. Etching by F⁻ is negligible and the SiO₂ etching rate is mainly determined by HF_2 species [17]. In order to get high selectivity towards SiO₂ with HF, the etch solution must restrain HF_2 species from being generated. One way to accomplish this is by adding an alcohol to the HF solution [18]. Another important parameter is the dielectric constant of the solvent. The lower the dielectric constant, the lower the silicon oxide etch rate will be because of lesser dissociation of HF. The better behavior of the HF/alcohol solutions may also be related to the surfactant properties of alcohols. Further, one can also eliminate the HF_2 reaction, by adding an acid to the HF solution [17]. The etching mechanism is then controlled by the pH of the solution. Figure 13 shows that each of the above-described components is really necessary to be able to etch high-k and

Electrochemical Society Proceedings Volume 2003-26

at the same time be selective to SiO_2 and silicon. The compositional ratio of all three compounds is optimized so that the highest selectivity towards thermal oxide and polysilicon is obtained. Etch rates, with the optimized etchant, for all layers under study are depicted in Figure 14.





Figure 13: Etch rate of implanted, thermally treated ALD HfO_2 , ThOx and polysilicon for a mixture of 1% HF, acid/HF, alcohol/HF or alcohol/HF/acid.

Figure 14: Etch rate for all layers under study when etched with 1% HF or with our optimized high-k etchant. (na.: not analyzed).



Figure 15: TEM pictures after gate electrode etch and after (left) high-k treatment and (right) wet removal of CVD HfO_2 (treated) with optimized high-k etchant.

Figure 15 shows TEM pictures to illustrate complete high-k removal and minimal Si recess (~ 1.1 nm) on patterned polysilicon/high-k gate electrodes with the developed approach. The approach involves a treatment of annealed CVD Hf-based films, followed by a selective wet removal. The treatment is actually a high-k layer damage by either ion bombardment from a plasma or ion implantation at low energies (Figure 15_left) of annealed films. After damaging, the high-k layer is removed selective towards most other layers exposed during processing (Figure 15_right). The developed chemistry is an HF-based wet chemical solution. The approach is discussed elsewhere into more detail [19].

CONCLUSIONS

The introduction of novel materials as gate dielectrics in future IC technologies will require adaptation of conventional cleaning, etching and surface preparation techniques. Initially, decent contamination monitoring will be required. For this, particular attention is given to TXRF analytics. Appropriate excitation energies and the related detection limits have been identified. We also distinguish the application of TXRF for Zr and Hf analysis on Si wafers on the one hand and the analysis of traces in the ZrO_2 and HfO_2 films on the other hand. Also cleaning strategies might have to be reconsidered as it is demonstrated that Zr and Hf poses a significant risk in wet cleaning processes where boundary layer neutralization occurs. This is related to the fact that both metals form hydroxides that have lowest solubility at neutral pH. It is demonstrated that either an all acid cleaning sequence or a HF based cleaning sequence exhibit the lowest cross contamination concern.

The relative importance of silicon surface pretreatment, prior to high-k deposition is elaborately discussed. The surface preparation is crucial to achieve good high-k layer growth, while its impact on the overall EOT of the gate stack should be minimized. In order to achieve this an ozone based surface preparation process has been developed and successfully demonstrated in transistors (achieving sub 1.0nm EOT).

Finally, from a transistor performance point of view, it is important to minimize silicon recess. Compared to conventional SiO₂, high-k materials are more resistant towards wet chemistries and require alternative removal strategies. We have developed a procedure to selectively remove high-k material from source/drain areas in devices. Improved selectivity for thermally treated high-k material can be obtained by damaging the layer. Once damaged, the layer can be removed selectively towards almost all other layers present during gate electrode patterning, by means of our developed etch mixture. This HF-based mixture also comprises an alcohol and acid for optimal selectivity towards oxides and silicon.

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STUDY OF THE EFFECT OF SILICON SURFACE TREATMENT ON EQUIVALENT OXIDE THICKNESS IN HIGH-K DIELECTRIC MOS GATE STACKS

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In this experiment, different surface treatments applied before mist deposition of high-k gate dielectrics (HfSiO₄) are investigated. Two different HfSiO₄ precursors are considered: stoichiometric and Hf-rich. It was found that *in-situ* UV/NO-last and anhydrous HF/methanol-last treatments result in lower EOT than *ex-situ* dilute HF-last or nitrogen plasma immersion treatments, regardless of film composition. TEM analysis shows thinner interfacial layer between high-k dielectric and Si substrate in the case of *in-situ* surface treatments. Results obtained emphasize the need for pre-high-k deposition surface treatment to be carried out *in-situ*.

INTRODUCTION

Recent studies on high-k dielectrics have focused on hafnium-based thin films due to its stability with Si substrate and high dielectric constant [1, 2]. In these studies, control of the interfacial oxide growth continues to be a key challenge. The impact of an interfacial oxide sandwiched between Si and high-k dielectric on electrical characteristics of MOS gate stacks is well recognized. Beneficial on one hand (superior electron mobility in the channel) and detrimental on the other (reduction of the capacitance of MOS gate stack), this interfacial oxide plays a critical role in defining both extend of capacitive coupling between gate and silicon as well as gate leakage current. It is, therefore, important that the effects controlling formation and properties of ultra-thin interfacial SiO_x in high-k MOS gate structures are well understood and controlled.

Our earlier experiments have demonstrated that mist deposition allows formation of fully functional ultra-thin high-k dielectric films [3]. The goal of this experiment was to characterize MOS gate structures in which high-k dielectric is formed by mist deposition and an interfacial SiO_x film grows in the course of post-deposition rapid thermal treatments of the Si wafer. The focus of this investigation was on the role Si surface treatments applied prior to high-k deposition play in defining interfacial oxide thickness, and hence, equivalent oxide thickness (EOT) of the high-k MOS gate stack.

EXPERIMENTAL

In this work, ultra-thin ($\leq 8nm$) HfSiO₄ films were mist-deposited from a liquid source on p-type (100) Si wafers using a commercial cluster tool [4]. The cluster includes three process modules: gas-phase surface preparation module, mist deposition module, and rapid thermal processing (RTP) module (Fig. 1).

Surface treatments investigated in this study include : (i) 100:1 dilute HF 3min dip, rinse/dry cycle applied ex-situ ("dHF-last" process), (ii) an in-situ anhydrous HF with methanol vapor ("AHF-last" process), (iii) sequence in which AHF process is followed in the same module by UV/NO exposure which re-grows about 0.5 nm thick, slightly nitrided (2.5 at% N2) oxide on the surface ("UV/NO-last" process) [5], and (iv) ex-situ nitrogen plasma immersion at 50 W plasma power ("N2PI" process). Following surface preparation, wafer is either loaded directly into deposition chamber, ex-situ treatments (i) and (iv), or transferred from the surface preparation module to deposition module in the ultra-pure N₂ ambient, in -situ treatments (ii) and (iii). During mist deposition, liquid precursor is converted into fine mist with droplet mean diameter of 0.25µm, and 2kV electric field is applied between wafer and field screen to attract the mist toward wafer surface. The liquid precursor for mist deposition contains n-octane mixed with Si 2-ethylhexanoate and Hf 2-ethylhexanoate. In this study, two different mixing ratios are used; stoichiometric HfSiO₄ mixture with Hf:Si=1:1, and Hf-rich mixture with Hf:Si=3:1. After mist deposition of high-k dielectric film, the wafer is subject to post-deposition anneal in RTP module. Thermal sequence consists of the following steps : 150°C 2min, 260°C 4min, 400°C 10min in nitrogen, and 4 spikeanneal at either 600°C or 700°C in nitrogen.



Fig. 1 Schematic diagram of cluster tool used in this study.

For electrical characterization, Pt gate contacts (area of 1.13×10^{-4} cm²) were deposited by e-beam evaporation on the high-k dielectric and Al film was evaporated for backside contact. Capacitance-voltage characteristics were measured at 1 MHz and

Electrochemical Society Proceedings Volume 2003-26

current density J was measured at -1V gate voltage. To determine reliability of deposited dielectrics, constant voltage stress (CVS) was applied in gate injection mode. Thickness of interfacial layer between high-k dielectric and Si substrate was measured by JEOL 2010F Field Emission Transmission Electron Microscopy (FE-TEM). Surface roughness was analyzed by Atomic Force Microscope (AFM), while film composition was analyzed by X-ray Photoelectron Spectroscopy (XPS).

RESULTS AND DISCUSSION

At first, ultra-thin HfSiO₄ films (about 8nm) were deposited using Hf:Si=1:1 precursor. Depositions were proceeded by various surfaces treatments and followed by spike-anneals at 700°C. Three different surface treatments were carried out prior to mist deposition: dHF-last, AHF-last, and UV/NO-last processes. Figure 2 shows C-V characteristics of MOS capacitors with HfSiO₄ gate dielectric stacks. As seen in this figure, UV/NO-last treatment yielded the highest capacitance density and lowest EOT value. The lowest capacitance density was found for dHF-last treatment.





The EOT of each film should be considered in conjunction with leakage current. Figure 3 shows EOT vs. leakage current density relation for 1:1 HfSiO₄ films for each surface treatment. Results from AHF-last and UV/NO-last treatment fall within HfO₂[6] and SiO₂[7] trend lines. Results after dHF-last treatment are very close to the values expected for SiO₂ gate oxide suggesting possibility of excessive growth of an interfacial SiO_x. In this case, high-k dielectric play a limited role in determining EOT value because overall EOT value is dominated by lower-k value of the interfacial SiO_x.

Interfacial layer of HfSiO₄ films deposited after UV/NO-last and dHF-last were compared by Transmission Electron Microscopy (TEM). In Figure 4, the interfacial layer in the case of dilute HF-last treatment was measured at 26Å, while that of UV/NO-last was 23Å. The thickness of HfSiO₄ film is 24 Å in both cases.

Electrochemical Society Proceedings Volume 2003-26



Fig. 3 EOT vs. leakage current density relation of HfSiO₄ films deposited after various surface treatments compared with HfO₂ [6] and SiO₂ [7], (dotted lines).

Observed difference in electrical properties can be explained not only by the difference in the thickness but also composition of the interfacial layer. Since the interfacial layer decreases the overall capacitance, thicker interfacial layer of dilute HF-last treatment results in lower capacitance, and hence, higher EOT thickness. UV/NO leaves slightly-nitrided layer on Si surface and suppresses further oxidation during post-deposition anneal [5]. As the result, UV/NO treatment leaves thinner interfacial layer between high-k dielectric and Si substrate, which is confirmed by TEM. Also, nitrided layer formed during UV/NO treatment, increases k-value of the interfacial layer and reduces EOT of overall dielectric stack. Therefore, EOT difference shown in Fig. 2 and Fig. 3 between UV/NO-last treatment and dHF-last treatment is contributed by difference in thickness and composition of interfacial oxide.



Fig. 4 Cross-sectional TEM photographs of interfacial layer and HfSiO₄ films deposited after dilute HF-last (left) and UV/NO-last (right) treatments.

In the continuation of this study HfSiO₄ precursor with 3:1 Hf:Si ratio and annealed at 600°C was investigated in conjunction with various surface pre-treatments. Physical thickness of deposited films was measured by ellipsometer at about 5nm. In

addition, yet another *ex-situ* pre-deposition surface treatment, wafer immersion in nitrogen plasma at plasma power less than 50W (N₂PI) was explored. This last step is meant to introduce nitrogen into a Si surface region which is expected to block excessive growth of interfacial SiO_x.

Figure 5 shows the C-V and J-V characteristics of $3:1 \text{ HfSiO}_4$ films deposited after various surface treatments. Again, UV/NO-last resulted in the highest current density, followed AHF-last process. Dilute HF and nitrogen plasma immersion resulted in the lowest capacitance density. As before (Fig. 2), capacitance values of two *in-situ* surface treatments are higher than those of two *ex-situ* surface treatments. Accumulation J-V characteristics show comparable leakage current density for AHF-last, dHF-last, and nitrogen plasma. UV/NO-last results in higher leakage current density than others by about an order of magnitude. This may be attributed to the slightly thinner interfacial SiO_x in this case.



Fig. 5 (a) C-V and (b) J-V characteristics of $HfSiO_4$ film deposited with Hf:Si = 3:1 precursor following different surface treatment.

Figure 6 shows EOT vs. leakage current density relation for $HfSiO_4$ films deposited after surface treatments. Within the same range of leakage current density, AHF-last treatment has the smallest EOT value. Again, UV/NO-last is superior in terms of EOT but it showed higher leakage current density than others, while AHF-last has lower EOT than two *ex-situ* methods at the same leakage current density. Nitrogen plasma does not seem to improve the electrical properties at all, but further investigation is needed to fully evaluate this approach.



Fig. 6 EOT vs. leakage current density relation of HfSiO₄ films deposited with Hf:Si 3:1 precursor.

Besides differences in the thickness of interfacial oxide different chemical composition also affects EOT of dielectric stack. Analysis of film composition by angle-resolved XPS did show difference in Hf atomic percentage depending on pretreatment, as shown in Table 1. UV/NO-last treatment resulted in clearly higher Hf atomic percentage than dHF-last. However, as seen in previous TEM photographs, HfSiO₄ phase of dielectric stack does not depend on surface treatment and has the same thickness regardless of the surface treatment method (Fig. 4). Therefore, it is postulated that difference in Hf atomic percentage come from the difference in interfacial oxide thickness. Since interfacial layer is expected to have less Hf in it, thicker interfacial layer after dHF-last treatment would lower the Hf atomic percentage of the overall film, and hence lower [Hf]/[Si] ratio. In HfSiO₄ film deposited after dHF-last treatment, [Hf]/[Si] ratio is 1.90 compared to 2.62 in the case of UV/NO-last. The XPS analysis result indicates that thicker interfacial layer formed after dHF-last treatment results in lower Hf atomic percentage and higher oxygen atomic percentage than in the case of UV/NO-last treatment.

Atom.%	Dilute HF last	Anhydrous HF last	UV/NO last
Hf	22.0	26.8	29.8
Si	11.6	11.9	11.4
0	66.4	61.3	58.8
[Hf]/[Si]	1.90	2.24	2.62

Table 1. Hafnium atomic percentage and [Hf]/[Si] ratio in Hf-rich HfSiO₄ Films.

The results observed in this study and illustrated in Figs. 2-5 involve complex interaction that includes: (i) effect of temperature on the thickness of interfacial oxide, (ii) effect of temperature on the chemical composition of interfacial oxide, (iii) effect of

Hf content in the high-k dielectric layer, and the last but certainly not the least is (iv) the effect of surface treatment. The last effect is the focus of this investigation but it cannot be considered without taking remaining three into account. In this context, the proposed interpretation of the results introduced above is as follows.

At first, in-situ surface treatment always results in lower EOT than ex-situ surface treatment. Although the final treatment was the same HF-last process, in-situ AHF-last treatment showed lower EOT than dHF-last. AHF is believed to produce a Si surface free of chemical oxide. Also, dHF leaves hydroxyl termination by water rinse and moisture that enhances oxidation during following thermal treatment. At the same time, in-situ UV/NO leaves nitrogen incorporated layer on surface and further suppress the growth of interfacial layer. Also, nitrogen in the interfacial layer results in the higher dielectric constant of interfacial layer and improves the EOT of overall dielectric stack. The same tendency was confirmed for the case of Hf-rich HfSiO4 also. However, it should be noticed that the effect of surface treatment seems to be less critical for 3:1 HfSiO₄ films annealed at 600°C than for 1:1 HfSiO₄ films annealed at 700°C. In the case of 3:1 HfSiO₄, the EOT difference between two surface treatments is smaller than that of 1:1 HfSiO₄. It is postulated that lower interfacial thickness in the case of 3:1HfSiO₄ would make the effect of surface treatment less visible because overall EOT mainly depends on the property of high-k layer. Since overall EOT becomes more dependent on the high-k thin film, thin interfacial oxide makes the overall EOT less dependent on the process condition that affects interfacial oxide growth. On the other hand, it is also possible that the interfacial oxide has slightly higher Hf concentration for the case of $3:1 \text{ HfSiO}_4$, and hence, higher dielectric constant. Higher k value of the interfacial oxide makes the overall EOT less dependent on the thickness of interfacial oxide laver. Therefore, the dependence of EOT value on surface treatment became less prominent in the case of 600°C annealed 3:1 HfSiO₄ as compared to 1:1 HfSiO₄ spikeannealed at 700°C.

Reliability of HfSiO₄ films deposited following different surface treatment was investigated with constant voltage stress mode. Gate electrode was biased at -3.85 V to inject the electron from gate to 8nm HfSiO₄ gate dielectric. Figure 8 shows the change in leakage current density with time during constant voltage stress. As seen in this figure, charge trapping related decrease of current as a function of time of stress was observed for all samples. However, gate dielectric stacks on dHF-last treated surfaces were experiencing catastrophic breakdown after about 10⁴ seconds of stress. Meanwhile, AHF-last and UV/NO-last displayed gradual wear-out after about 200 seconds of stress. The difference in wear-out time is possibly related to the thickness of interfacial SiO_x. UV/NO-last treatment showed the highest leakage current, and hence, the largest amount of electron is injected through the overall dielectric stack during the test. Thick interfacial SiO_x in the dHF-last case is probably a reason for apparently higher resistance to electric field stress in this case.



Fig. 7 Change in leakage current density with time of constant voltage stress of HfSiO₄ gate dielectrics.

SUMMARY

This experiment demonstrated that surface treatment before $HfSiO_x$ high-k dielectric formation plays an important role in determining final electrical characteristics of the gate stack formed by mist deposition. *In-situ* AHF-last treatment and UV/NO-last treatment result in higher final capacitance of the gate stacks. TEM and XPS analysis revealed that thinner and more Hf-rich interfacial oxide is formed after UV/NO-last treatment. Thicker interfacial SiO_x in the case of dHF-last treatment is responsible for higher resistance of the gate stack to electrical field stress, but at the same time results in the higher EOT value than *in-situ* surface treatments investigated.

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ATOMIC LAYER DEPOSITION OF SILICON NITRIDE BARRIER LAYER FOR SELF-ALIGNED GATE STACK

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The surface chemical processes needed to optimize subsequent deposition steps and to grow self-aligned structures have been investigated for gate dielectric formation. UV-Cl₂ exposures were used to terminate bare silicon surfaces with chlorine atoms (10% Cl₂ in N₂ at 150°C and 100 Torr for 10 min, 1000 W Xe arc lamp). Exposure to NH₃ and UV-NH₃ chemistries (10% NH₃ in N₂ at 80°C for 10 min) replaced the chlorine atoms with amine (–NH₂) groups, intended as the foundation of a silicon nitride diffusion barrier. By providing a more reactive surface, ALD of silicon nitride occurs at lower temperatures (<100°C) and with better initial deposition rates compared to deposition on hydrogen terminated silicon. Surface activation by UV-Cl₂ is selective for Si over SiO₂, enabling deposition of self-aligned nitride and dielectric films. The amine surface coverage saturates at less than one monolayer and is equilibrium limited. UV illumination increased amine coverage at similar conditions.

INTRODUCTION

The candidate high-k gate materials for the replacement of silicon dioxide are oxides and alloys (silicates) of transition metal cations, with Hf and Zr the most likely candidates. These materials must be deposited using physical or chemical processes, rather than grown in place by consuming part of the surface as is done for a silicon dioxide gate. The new materials and deposition mechanisms will require more stringent surface preparation to ensure an adequate interface between the substrate and deposited dielectric. The silicon surface should be terminated to protect against adventitious adsorption of contaminants and to promote deposition of the high-k layer. Dry cleans offer a means to both clean a surface and controllably vary the surface termination *in situ*.

Two approaches are under active investigation to form gate dielectrics using higher permittivity (k ~ 20) metal oxides with the common goal being to produce a gate dielectric film with the lowest overall equivalent oxide thickness (EOT). In the stacked layer approach, a diffusion barrier is formed at the silicon surface on top of which the metal oxide gate material is deposited, and in the single layer approach, a metal oxide or metal silicate layer is deposited directly on the silicon surface (1-6). The single layer approach employs a metal silicate (M_xO_y)(SiO₂)_z (where M = Zr, Hf, Y, La) directly on the Si substrate without a buffer layer. The dielectric constant of these silicates is lower than the corresponding metal oxides, yet the EOT is often smaller for the single layer silicate than the stacked passivation and metal oxide layers (7). The EOT is proportional to physical thickness divided by the dielectric constant. Since the dielectric constant of the passivation layer is much lower than either the metal oxide or the silicate, it typically dominates the EOT even though its thickness may be much less. Silicates consequently

give up some value in the dielectric constant to the metal oxides but can produce a smaller EOT compared to stacked metal oxide/barrier layer structures. To achieve the lowest EOT, the passivation layer must be thin; no more than one or two monolayers.

Atomic Layer Deposition (ALD) holds the promise of depositing conformal, pin hole free layers with atomic scale control, well suited to deposition of both thin diffusion barrier layers and the high-k dielectric material. Current ALD processes, however, saturate the surface without depositing complete layers during each cycle, resulting in deposition of only 1/10 to 1/3 of a layer per cycle. Each cycle consists of a sequence of: dose precursor A, purge, dose precursor B, purge. Each step requires from 2-4 s each, so 3-10 AB cycles lasting from 24-80 s would be needed to deposit one 5Å thick layer. Moreover, nucleation of films on the starting surface is an issue that has not been addressed. Steve George at the University of Colorado found that nucleation of a tungsten layer on a hydroxylated silica surface using ALD required approximately 10 AB cycles (8). ALD is consequently an emerging technology that holds the promise of precise control of diffusion barrier and high-k films, but the growth of films using this method is incompletely understood. The surface preparation methodology currently used prior to deposition of alternative gate films has been more or less borrowed from conventional SiO₂ gate formation or silicon epitaxial growth, where the goal is to obtain a Hterminated silicon surface (9, 10). By using gas phase processes to controllably alter the silicon surface termination, the surface reactivity can be increased, reducing the number of deposition cycles required to reach monolayer growth.

Silicon Nitride Diffusion Barrier layer

To prevent the formation of a permittivity-lowering silicate, a thin (one or two monolayers) silicon nitride diffusion barrier can be grown prior to deposition of the metal oxide dielectric layer. The proposed deposition sequence, as shown in Fig. 1, starts with



Figure 1: Proposed ALD sequence for deposition of silicon nitride diffusion barrier layer and hydroxyl priming layer to prevent silicate formation and to promote adhesion of high-K dielectric. (A.) NH_3 participates in reaction with surface chlorine atoms to deposit surface amine (-NH or - NH_2) groups (B.) and evolve HCl. (C.) The nucleophilic electron pair of the amine group attacks the silicon of SiCl₄, adding another layer of silicon nitride bonds and again generating HCl. The surface (D.) is chlorine terminated so step A can be repeated to deposit another silicon nitride layer, or H₂O can be introduced (E.), with the oxygen attacking the Si-Cl bond and making silanol (Si-OH) groups (F.).

Cl terminated silicon. Upon exposure to ammonia (NH_3) vapor, the Cl picks up a hydrogen to make HCl and leaves the first layer of nitride bonds in the form of amine groups. A silicon bearing reactant, such as SiCl₄ is then introduced. The nucleophilic electron pair on the surface amines reacts with the silicon in SiCl₄, again making HCl and adding a second layer of silicon nitride bonds. The SiCl₄ exposure regenerates a chlorinated surface, so the cycle could be repeated to increase the thickness of the nitride layer, or the chlorine can serve as a leaving group for the deposition of a different precursor.

High-k Dielectric

A logical interface between the metal oxide dielectric (HfO₂, ZrO₂, etc) and the substrate would consist of a monolayer of oxygen to serve as a silicon-oxygen-metal bridge. A monolayer of SiO₂ would be unreactive towards deposited layers, but a monolayer of hydroxyl-terminated silicon (silanol) would be able to participate in further reactions. In the case of HfO₂ deposition, HfCl₄ could be introduced, with the Cl again reacting with the hydrogen to release HCl and creating a -Si-O-Hf- bridge. The hafnium surface is still Cl terminated, so the second half-reaction can commence using H₂O to regenerate a hydroxyl terminated surface. The cycle of HfCl₄-H₂O exposures can repeat as many times as necessary to grow the desired film thickness.

Self-Aligned Gate Stack

By preparing the surface with a reactive terminating species, the activation energy of the deposition reaction is lowered allowing deposition to occur at less than 100° C rather than 300 to 500°C (9-11). If the ALD sequence is then initiated at 100° C, deposition only occurs at the surface sites that have been activated, leaving other surfaces unaffected. The UV-Cl₂ surface treatment readily terminates bare Si surfaces with Cl



Figure 2: Process sequence illustrating possible route to deposition of a self-aligned gate stack. (A.) Wafer is annealed to drive off hydroxyl groups initially present on the oxide to prevent their reactions with metal precursor in step F. (B.) UV-Cl₂ removes organics and metals and displaces fluorine from the silicon surface. (C.) Chlorine leaving group terminates the bare silicon before NH₃ exposure. (D.) Nucleophilic electron pair on the amine group attacks Si of SiCl₄. (E.) Nucleophilic attack by the oxygen in H₂O on surface silicon atoms results in hydroxyl terminated nitride layer. (F) Selective atomic layer deposition (ALD) of gate dielectric proceeds, depositing high-*k* material over gate regions and not on oxide surfaces.

atoms, but is unable to alter SiO₂. This selectivity can be used to guide the patterned deposition of dielectric films without using sacrificial masking layers. If the gate pattern has been etched through the field oxide to the underlying silicon substrate, then that pattern can be reused to govern the deposition of the gate stack, i.e., the diffusion barrier, the priming interface, and gate dielectric layers. As diagrammed in Fig. 2, the first step of the self-aligned gate stack sequence is deactivation of the oxide surfaces (A), for which a high temperature anneal has been proposed. Silanol groups will be intentionally grown as the priming layer, and hydroxyls are used during the dielectric deposition as reactive sites for reaction with HfCl₄ (or ZrCl₄, etc.). To prevent HfO₂ from growing on the oxide surfaces, any hydroxyls on SiO₂ surfaces must be removed prior to surface activation. Surface preparation then proceeds, finishing with a UV-Cl₂ cleaning step that also leaves the silicon terminated with Cl atoms (B). If a nitride barrier layer is required, the sequence would include a NH_3 exposure (C) followed by $SiCl_4$ (D) to grow the nitride barrier shown in Fig. 1, or the sequence could go straight to the H₂O exposure (E) to put down the hydroxyl priming layer. Because the wafer has been annealed, the oxide surface is now hydrophobic and therefore unaffected by the H₂O vapor. Because each halfreaction of the ALD sequences is surface selective, deposition of the dielectric (F) can continue until the desired film thickness has been achieved and no material will be



Figure 3: XPS spectra showing growth of N 1s peak after Cl terminated silicon surface (10% Cl₂ in N₂ at 100 Torr and 150°C for 10 min.) was exposed to 10% NH₃ in N₂ at 100 Torr and 80°C for 10 min. (Post NH₃). When NH₃ exposure occurred under UV illumination (1000 W Xe arc lamp), nitrogen coverage increased from ~0.35 ML to ~0.5 ML (Post UV-NH₃).

deposited on the field oxide.

EXPERIMENTAL RESULTS

All experiments were performed the Research Cluster Apparatus on (RCA), a collection of gas phase reactors connected by a high vacuum transfer tube to a surface analysis chamber equipped with x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Among the reactor modules is the photochemistry reactor where samples were exposed to NH₃, UV-Cl₂, and other halogen chemistries. The in situ capabilities provided the means to process and characterize a surface without exposing it to ambient conditions. Gas phase surface preparation steps enabled Si to be terminated with a specific atom or functional group by virtue of vacuum isolation (10^{-9} Torr) between modules. This capability allowed a study of how termination influences the subsequent deposition process.

Electrochemical Society Proceedings Volume 2003-26



Figure 4: Saturation Coverage of N on Cl terminated silicon surface as function of NH_3 partial pressure. All Exposures were 10 minutes at 75 to 80°C. Total pressure and NH_3 concentration varied.

Cl-terminated Si(100) (p-type, 38 -63 ohm-cm) samples were prepared with 10 min exposures to 10% Cl₂ (Air Products Chemicals, Inc., VLSI grade, and 99.998%) in N2 mixtures at 100 Torr and 150°C under illumination of a 1000 W Xe arc lamp equipped with an infrared filter to limit sample heating. Fig. 3 shows the XPS spectra from a Cl terminated Si sample before and after exposure to 10% NH₃ in N₂ at 100 Torr and 80°C for 10 minutes. The N 1s peak at 398 eV indicated the growth of silicon nitride groups on the surface with coverage estimated at 35% of a monolayer. The Cl 2s peak decreased, but was not eliminated, indicating the surface reaction depicted in Fig. 1 did not go to completion. Time experiments indicated the nitride layer saturated in less than 4 minutes at 23°C. The reactor was not

optimized for shorter reaction times. Fig. 4 shows the saturation coverage of N as a function of NH_3 partial pressure. Nitrogen was deposited on Si surfaces using NH_3 only with UV-Cl₂ pre-treatments. When another Cl terminated Si sample was exposed to NH_3 at the same conditions but under UV illumination, the coverage increased to approximately 50% of a monolayer. In both cases, there was an increase in the O 1s peak, attributed to water contamination in the NH₃ bottle (MG Products, 99.99%). There was also an increase in adventitious carbon after UV exposure.



Figure 5: Modified reaction sequence for demonstration of silicon atom addition to nitride layer, substituting trimethylchlorosilane (TMCS) for silicon tetrachloride (SiCl₄). The additional UV-Cl₂ exposure is necessary to activate the otherwise unreactive methyl groups.

To demonstrate the second step of the barrier layer ALD sequence in which a Si atom is added to the surface amine $(-NH_x)$ groups, a modified sequence substituting trimethylchlorosilane (TMCS) for SiCl₄ was performed (Fig. 5). The UV-Cl₂-NH₃-TMCS

sequence was completed twice for the same sample (Fig. 6). After the first TMCS exposure, the N 1s signal decreased slightly, as would be expected if a $-Si(CH_3)_3$ group attenuated N 1s photoelectrons. After the second UV-Cl₂ treatment, the N 1s signal was attenuated even further, suggesting that the N 1s photoelectrons were attenuated by



Figure 6: XPS spectra of single sample after two cycles of UV-Cl₂, NH₃, TMCS exposures. N 1s peak (398 eV) decreased slightly after TMCS exposures, but decreased significantly after 2nd UV-Cl₂ treatment. Second NH₃ exposure resulted in larger N 1s peak than first NH₃ exposure.

-Si(CCl₃)₃ groups. The second NH₃ exposure resulted in a significantly larger N 1s peak, attributed to the increased number of bonding sites on the -Si(CCl₃)₃ terminated surface. Though not conclusive, the trends illustrated in the XPS spectra are consistent with the proposed reaction sequences.

The ultimate goal is to deposit a silicon nitride barrier layer that is continuous over a large area and one or two atoms thick with a surface termination that provides the means to grow a self aligned high-k dielectric film.

DISCUSSION

The goals of the nitridation experiments were to lower the activation energy of the deposition reaction and provide a means to achieve layer-bylayer growth by terminating the surface with reactive leaving groups. It is the lowered activation energy for reactions

on the activated surfaces relative to non-activated surfaces that makes the self-aligned gate stack feasible. The leaving group (Cl) readily bonds with an H atom on NH₃, making the thermodynamics more favorable for a Cl terminated surface than with an H terminated surface. This shifts the reaction equilibrium towards deposition and is expected to eliminate the typical 10-20 cycle lag currently required to initiate film growth. Ammonia did not react with H-terminated Si under the conditions of the experiments. To effectively serve as a diffusion barrier, the film must be free from pinholes even when the overall film thickness is only one or two layers thick; increasing the surface reactivity will help to ensure all sites are filled. A similar situation applies to the interface of the dielectric films with the diffusion barrier layer. The deposition of HfO₂ films grown on H-terminated silicon initiates slowly because the HfO₂ forms islands on the surface, rather than a continuous film (11). Reaction of the HfCl₄ with the silanol adhesion layer is more thermodynamically favorable than reaction with a H-terminated surface, which could improve nucleation and reduce islanding.

As indicated by the remaining Cl 2s and 2p peaks in the XPS spectra, the NH_3 exposures failed to completely replace Cl at all bonding sites. N coverage did not increase with time, indicating the reaction had proceeded to saturation, but the N coverage did increase with the partial pressure of NH_3 , suggesting that the reaction equilibrium and not surface site selectivity or steric effects determined the saturation limit. If the presence of HCl drives the equilibrium of the reaction shown in Fig. 1A

backwards, then the UV-Cl₂ steps in Fig. 7E may have generated HCl, driving the desorption of the nitrogen groups and potentially accounting for the decreased N 1s peak of the second UV-Cl₂ spectrum in Fig. 7.

Ultraviolet photons with a wavelength less than 280 nm photodissociate NH_3 to NH_2 , and photons below 224 nm generate NH fragments (12). UV activated NH_3 reacted with a H-terminated silicon surface but the coverage was lower than on a Cl-terminated surface; no reaction with H-terminated silicon was observed without UV. The inherent instability and high reactivity of the photofragments shifted the equilibrium coverage toward products for the UV-NH₃ process.

CONCLUSION

As the microelectronics industry works to find a replacement for SiO_2 gate dielectrics, new cleaning and surface termination techniques will have to be developed to ensure a satisfactory interface between the silicon substrate and the high-*k* gate dielectric material. Gas phase cleaning processes can be integrated into single wafer cluster tools, allowing the wafer to go from etching to surface preparation, and then directly to deposition without leaving vacuum. Gas phase cleans also have the advantage of controllably altering the silicon surface termination to make the surface more reactive with subsequent deposition chemistries. By terminating the Si with Cl, deposition of the silicon nitride barrier layer can proceed by ALD at lower temperatures than if the surface were hydrogen terminated. This work aims to improve nucleation of the nitride films to allow deposition to begin at near-monolayer-per-cycle rates and to form more complete layers free of pinholes. The selectivity of the UV-Cl₂ process could also enable deposition of self-aligned diffusion barrier layers for transistor gate stacks. Currently, the nitride coverage is equilibrium limited, and requires more work to identify reaction conditions favorable to complete monolayer formation.

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Electrochemical Society Proceedings Volume 2003-26

SUB-NANOMETER HIGH-K GATE STACK SCALING USING THE HF-LAST/NH₃ ANNEAL INTERFACE

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ABSTRACT

The scaling of high-k gate stacks using an HF-last/NH₃ anneal bottom interface was evaluated for EOT, Nit, and mobility effects on HfO₂/polysilicon and HfO₂/metal gate transistors. TEM analysis of HFlast/NH₃ bottom interface layers was also done, showing HF-last/NH₃ and O₃ bottom interface layer thickness to be identical within the resolution of the measurement. Electrical characterization showed that use of HFlast/NH₃ anneal bottom interface reduces the EOT of high-k/polysilicon gate devices by 0.3 nm and high-k/metal gate devices by about 0.15-0.2 nm with respect to the corresponding ozonated (O_3) interface sample. Charge pumping on the HF-last/NH₃ anneal bottom interface indicated N_{it} density of $\sim 5 \times 10^{10}$ cm⁻², slightly greater than the O₃ interface control, with mobilities nearly equivalent to those in corresponding O₃ interface devices. These data show NH₃ bottom interface chemistry to be highly effective in scaling the EOT of HfO₂/polysilicon and HfO₂/metal gate stacks while giving nearly equivalent electrical characteristics in transistors fabricated using this method.

INTRODUCTION

High-k gate stacks are an integral part of device features needed to meet performance requirements for the 65 nm technology generation and beyond. The International Technology Roadmap for Semiconductors (ITRS) predicts that devices manufactured beginning in 2004 can require an equivalent oxide thickness (EOT) of less than 1 nm, while requiring gate leakage values far below that which can be obtained when using SiO₂ for the gate dielectric ^[11]. Using high-k materials such as HfO₂ as a substitute gate dielectric is a solution ^[2], however typical high-k gate stacks require a SiO_X bottom interface, such as the ozonated (O₃) interface ^[3], in the high-k transistor gate stack to provide increased mobility and operating currents (Id_{1,sat}) ^[4]. Unfortunately, the electrical thickness of the SiO_X bottom interface may consume a majority of the 1 nm EOT budget. As EOTs scale below 1 nm, it is therefore critical that these bottom interface layers be minimized while retaining favorable electrical characteristics. In this work, the authors demonstrate an alternate approach to the standard O₃ bottom interface, in which the HF-last/NH₃ anneal bottom interface is evaluated as a means to reduce the

Electrochemical Society Proceedings Volume 2003-26

high-k transistor gate stack to sub-nanometer EOT, with approximately equivalent mobility characteristics to the O₃ bottom interface.

DESCRIPTION

NMOS transistors were fabricated on 200 mm p-type epitaxial <100> Si wafers using atomic layer deposition (ALD) of HfO_2 dielectric followed by either polysilicon or TiN/polysilicon gate electrodes. Prior to HfO_2 deposition, the substrates were given either O₃ or HF-last/NH₃ anneal pre-treatment as follows

i) O₃ pre-treatment: HF/HCl – O₃/HCl, or
ii) HF-last/NH₃ anneal pre-treatment: HF/HCl – O₃/HCl – HF – NH₃.

All cleaning was performed on a commercially available DNS FC-821L advanced wet cleaning tool utilizing single pass chemistry usage. The wafers remained on a robotic quartz lifter in the bath and fresh DI water and chemicals were injected into the tank. At the completion of the injection, the wafers sat for a pre-determined amount of time and were then rinsed in-situ.

After organic material clean using a sulfuric peroxide mixture, HF/HCl etch was done using 200:1 DI:HF and was targeted to remove 200 Å of thermal oxide; HCl was added at a concentration of 0.2%. During the O₃ clean, O₃ was dispensed for 10 minutes at 23°C with a concentration of 20 ppm; HCl was also added at this step to a concentration of 0.2%. In the NH₃ pre-treatment, all of the previous steps were done followed by an HF oxide removal and NH₃ interface treatment. The NH₃ processing was performed at 700°C, 30 Torr, for 15 seconds.

In order to characterize the effect of HF-last/NH₃ anneal vs O₃ interface treatment over a range of high-k thickness, HfO₂ was varied from approximately 22 Å (40 cycles) to 30 Å (55 cycles). Mobility and charge pumping characterizations were performed on transistor structures, while EOTs were measured on capacitor structures fabricated during the transistor flow using NCSU CVC modeling ^[5]

For TEM, the finished transistors were prepared by low-angle ion milling with final thinning by a 2.5 kV Ar ion beam at a shallow angle to the x-section surface. TEM analysis was done at an energy of 300 keV with the sample aligned to the [110] plane of the silicon substrate. Using this setup, the TEM has a resolution limit of about 0.2 nm.

RESULTS AND DISCUSSION

The EOT of HF-last/NH₃ anneal gate stacks was found to be reduced with respect to the standard O₃ interface gate stacks. Figure 1 shows capacitance-voltage (C-V) curves of HF-last/NH₃/55cycle HfO₂/poly and O₃/55cycle HfO₂/poly gate stacks, showing higher capacitance in the HF-last/NH₃ interface than in the O₃ interface. Figure 1 also shows the EOT and V_{fb} as modeled using CVC.

Electrochemical Society Proceedings Volume 2003-26



Figure 1 – Capacitance vs Voltage of HF-last/NH₃/55cycle HfO₂/polysilicon (solid line) and O₃/55cycle HfO₂/polysilicon (dashed line) gate stacks. EOT and V_{fb} are also shown.

In agreement with higher capacitance values, CVC modeling shows the HF-last/NH₃ anneal gate stack to have an EOT reduced by 0.3 nm when compared to the O_3 interface gate stacks. Similar data comparing HF-last/NH₃ anneal and O_3 interface EOTs over multiple wafers and production lots is shown in Figure 2.



Figure 2 – EOT effect of HF-last/NH₃ anneal vs O_3 bottom interface for polysilicon (filled symbols) and TiN/polysilicon (non-filled symbols) gate electrodes. Note that the HF-last/NH₃ anneal reduces EOT by 0.15-0.3 nm vs the O_3 bottom interface.

95

From Figure 2 it is seen that the EOT reduction which occurs as a result of using HFlast/NH₃ anneal in place of the O₃ interface can range from 0.15 nm to 0.3 nm depending on other elements of the gate stack such as anneals, the gate dielectric thickness, and choice of gate electrode material. Data on polysilicon gate electrodes from multiple wafers and lots (filled symbols in Figure 2) shows that the EOT for the HF-last/NH₃ anneal interface is reduced by about 0.3 nm compared to the equivalent O₃ interface. Data on TiN/polysilicon electrodes over multiple wafers and lots (non-filled symbols in Figure 2) shows that the NH_3 interface is reduced by about 0.15-0.2 nm compared to the equivalent O₃ sample.

TEM analysis of these gate stacks has been done to make a comparison of physical thickness in HF-last/NH₃ anneal and O₃ interface gate stacks. Figure 3 shows TEM micrographs of the gate stack cross-section as well as EOT and the bottom interface thickness averaged for several samples.

HF-last/NH₃ Anneal/HfO₂/TiN/poly O₃ /55cycle HfO₂/TiN/poly EOT = 0.96 nm EOT = 1.16 nm elel Bottom Bottom Interface Interface Laver INTAL Javer Hfe Bottom Interface = 0.93 nm Bottom Interface = 0.96 nm

(a)

(b)

Figure 3 - EOT, TEM micrograph, and averaged bottom interface thickness of (a) HF-last/NH₃ anneal/55cycle HfO₂/TiN/poly, and (b) O₃/55cycle HfO₂/TiN/poly gate stacks.

From Figure 3 the averaged TEM thickness of the HF-last/NH₃ anneal interface (0.93 nm) is shown to be equal to that of the O₃ interface thickness (0.96 nm) within the resolution of the TEM measurement. Figure 3 also shows the EOT of each respective

Electrochemical Society Proceedings Volume 2003-26
gate stack, showing the EOT of the HF-last/NH₃ anneal gate stack is reduced by 0.2 nm when compared to the O_3 interface gate stack. Since Figure 3 shows the physical thicknesses are nearly equivalent, the EOT difference must be primarily due to material differences in the respective gate attacks. Figure 4 shows results of high-angle annular dark field (HAADF) scanning TEM (STEM) electron energy loss spectroscopy (EELS) showing the relative Nitrogen levels for the gate stacks of Figure 3.



Figure 4 – HAADF-STEM EELS showing relative levels of N in HF-last/NH₃ anneal/55cycle HfO₂/TiN/poly (solid line) and O₃/55cycle HfO₂/TiN/poly (dotted line) gate stacks (X-axis is diagonal to gate stack depth).

Note that Figure 4 shows that the level of N is relatively higher in the HF-last/NH₃ anneal bottom interface as compared to the O_3 interface layer, resulting in an increased the k-value of SiO₂ dielectric in HF-last/NH₃ anneal bottom interface. Although other effects may be present, this data indicates the EOT difference can primarily be attributed to enhanced N incorporation in the HF-last/NH₃ anneal bottom interface (as compared to the O_3 interface layer), resulting in increased k-value for the SiO₂ interface.

A series of electrical measurements were also performed on these gate stacks to evaluate the effect of the HF-last/NH₃ anneal on the bottom interface quality. Mobilities of HF-last/NH₃ anneal gate stacks were not degraded. Figure 5 displays the a comparison of mobility for HF-last/NH₃/55cycle HfO₂/poly and O₃/55cycle HfO₂/poly interface gate stacks; the universal curve for SiO₂ is also shown in Figure 5.

97



Figure 5 –Mobility vs. Electric Field for HF-last/NH₃ anneal and O₃ bottom interface showing nearly equivalent mobilities.

Note from Figure 5 that the mobilities for these transistors are nearly equivalent. Charge pumping was also done on HF-last/NH₃ anneal and O₃ interface gate stacks to determine what effect the HF-last/NH₃ anneal has on interface density (N_{it}). Figure 6 shows a plot of 1MHz N_{it} for HF-last/NH₃ anneal and O₃ interface gate stacks.



Figure 6 - 1 MHz Charge trapping results for HF-last/ NH_3 anneal and O_3 bottom interface gate stacks.

Electrochemical Society Proceedings Volume 2003-26

Note that although Figure 6 shows the HF-last/NH₃ anneal interface has about four to five times the measured interface trap density as the O_3 interface, both gate stacks show relatively low N_{it} in the 10^{10} cm² range. At these low N_{it} levels, interface traps do not appear to limit the device mobilities, however, since the data of Figure 5 show the transistor mobilities to be nearly equivalent for the HF-last/NH₃ anneal and O_3 pre-interface cases.

SUMMARY

In conclusion, we have shown that use of the HF-last/NH₃ anneal bottom interface reduces the EOT of high-k/polysilicon gate devices by 0.3 nm and reduces EOT of TiN/polysilicon gate devices by about 0.15 nm compared to the equivalent O₃ interface sample. TEM and HAADF EELS indicates the decrease in EOT is primarily due to N enhancement in the HF-last/NH₃ anneal bottom interface, and not to differences in physical thickness of between the HF-last/NH₃ anneal bottom interface and the O₃ bottom interface. Our data show mobility to be comparable for HF-last/NH₃ anneal and O₃ bottom interface transistors, although charge pumping measurements indicate the HF-last/NH₃ anneal interface to have a higher trap density.

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Electrochemical Society Proceedings Volume 2003-26

IMPROVEMENTS IN ADVANCED GATE OXIDE ELECTRICAL PERFORMANCE BY THE USE OF AN OZONATED WATER CLEAN PROCESS*

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The clean performed prior to gate dielectric formation has traditionally involved variations of Standard Clean-1 (SC1) and Standard Clean-2 (SC2). These formulations mix hydrogen peroxide (H_2O_2) with ammonium hydroxide (NH₄OH) or hydrochloric acid (HCl) at various temperatures and concentrations. Since 1990, researchers have been investigating the use of ozonated water as an alternative to the SC1-SC2 chemical sequence. Ozonated water is of interest as a way to potentially reduce chemical usage, lower cost, and improve clean performance.

This work compares a clean using ozonated water (O_3) to cleans utilizing SC1 and SC2. Devices with 21 Å gate dielectric oxides are used to identify the impact of the clean on transconductance, saturation current, and mobility. This paper also proposes explanations for observed performance differences.

INTRODUCTION

The Equivalent Oxide Thickness (EOT) of MOS devices is being scaled aggressively to meet the requirements of the ITRS roadmap. This is being accomplished through the use of ultra thin SiO_2 gate dielectrics and high dielectric constant layers such as HfO₂, HfSiO₂, and HfSiON.

As device sizes shrink, the importance of the silicon-dielectric interface increases. Correspondingly, the pre-gate clean becomes increasingly critical as it directly impacts the interface. The pre-gate clean can impact metallic contamination level, interface roughness and the quality of the chemical oxide present when dielectric formation begins.

In this work, three different clean sequences were tested and compared. Two of the clean sequences were based upon the conventional SC1 and SC2 chemistries used in the industry since the 1970's [1]; the other clean involved ozonated water, as proposed by MEMC in 1990 [2]. Cleaning with ozonated water has been studied for some time [3], but has not yet gained widespread acceptance for pre-gate applications.

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Electrochemical Society Proceedings Volume 2003-26

EXPERIMENTAL

Transistors of varying dimensions were manufactured to allow an evaluation of pre-gate clean impact on device performance and reliability. These NMOS structures were created on 200 mm p/p+ epi substrate.

All cleans were performed using a commercially available DNS FC-821L advanced wet tool with single pass chemistry. Wafers were held by a robotic quartz lifter in the bath, while fresh deionized (DI) water and chemicals were injected into the tank. At the completion of the injection, the wafers soaked for a pre-determined time and were then rinsed in-situ.

Cleaning sequences evaluated in this study were:

- 1. HF/HCl followed by O₃/HCl
- 2. HF/HCl followed by SC1 followed by SC2
- 3. HF followed by SC1 followed by SC2

The HF etch portion of all sequences had a formulation of 200 parts water to 1 part 49% HF and was targeted to remove 200 Å of thermal oxide. When included, HCl was added at a concentration of 0.2% by volume. Ozonated water (from an MKS Liquozon 100 ozone generator) was dispensed for 10 minutes at 23°C with the ozone concentration set to 20 ppm. All SC1 dispenses had a formulation of 50:1:1 (H₂O:H₂O₂:NH₄OH) and were run at 65°C for 7 minutes. All SC2 dispenses had a formulation of 50:1:1 (H₂O:H₂O₂:NH₄OH) and were run at 23°C for 7 minutes. At the completion of each clean sequence, wafers were transferred to the dryer module, where they received a 3-minute rinse in DI water, and a low pressure IPA/hot N₂ dry.

To remove organic contaminants, all wafers were processed through a mixture of sulfuric acid and hydrogen peroxide (SPM) prior to processing through the pre-gate clean. Upon completion of each clean split, the wafers were processed with minimal queue time (less than 10 minutes) through a 21 Å in-situ steam generated (ISSG) oxidation process on an Applied Centura.

Transistor wafers were automatically tested at the end of the line to collect electrical data. Testing was performed on 17 die per wafer. On each die, transistors with a 10- μ m gate width were measured at gate lengths varying between 0.15 μ m and 1 μ m. For measurements of transconductance (G_m), the supply voltage (V_d) was set equal to 50 mV. For measurements of saturation current (I_{dsat}), the supply voltage (V_d) was set equal to the gate voltage (V_g) at a value of 1.8 V, and threshold voltage (V_t) was obtained through linear extrapolation. At the completion of the automated testing, manual capacitance-voltage (C-V), current-voltage (I-V), and drain current – gate voltage (I_d-Vg) measurements were made on a 20 μ m x 20 μ m transistor.

The data obtained was entered into the North Carolina State University (NCSU) CVC model to calculate EOT and flatband voltage (V_{fb}) values. Oxide thicknesses (T_{ox}) were calculated from C-V data, taking into account quantum corrections in which the methodology defined by J. Hauser was utilized [4]. The I-V data and the output from the CVC model were then input into the Hauser NCSU mob2d mobility model from which values were obtained for mobility, surface roughness, and interface scattering.

RESULTS

Figure 1 shows transconductance values obtained from the different clean splits. The data shows higher transconductance values when O_3 is used than when SC1 and SC2 are used. The results also suggest that the addition of HCl to HF improves transconductance. In Figure 2, saturation currents are shown. Again, the O_3 split shows better performance, while the SC1-SC2 sequence without HCl in HF is inferior.



Figure 3 shows the effective mobility curves that were generated from the NCSU mobility model. The data suggests that the O_3 clean results in mobility that is considerably higher than when SC1 and SC2 are used. For cleaning sequences that include SC1 and SC2, mobility is improved if HCl is added to the HF step.



Figure 3 Effective Mobility

Table 1 shows two values extracted from the NCSU model: roughness (length*height) and interface scattering. The data suggests that the O_3 process led to the smoothest surfaces; the SC1-SC2 process that did not incorporate HCl into the HF had the roughest surface and the highest level of interface scattering.

Clean Split	Roughness (Å ²)	Interface Scattering (#/cm ²)
HF/HCl - O₃/HCl	27.21 (st dev = 0.38)	3.36E+10 (st dev = 4.6E+09)
HF/HCl - SC1- SC2	30.22 (st dev = 0.55)	4.94E+10 (st dev = 1.6E+09)
HF - SC1 - SC2	33.74 (st dev = 0.26)	8.31E+10 (st dev = 8.1E+09)

Table 1 Roughness and Interface Scattering Data from NCSU Mobility Model

Other researchers have also observed that the addition of HCl to HF can improve roughness. Tardiff, et al. measured roughness using AFM and found that HCl addition reduced microroughness [5]. Tardiff speculated that HCl shifted the concentration of ionic species in solution by reducing pH; at lower pH values, there is less of the silicon-etching HF_2^- species in solution.

While the inclusion of HCl in HF improved device performance, results were best for the clean sequence that included O_3 . Results suggest that the O_3 clean leads to less roughness, less interface scattering, higher mobility, and higher saturation current than the SC1-SC2 clean sequences.

DISCUSSION OF MECHANISM

It was suspected that the very dilute 50:1:1 SC1 formulation led to microroughening of the wafer surface in the non-O₃ splits. NH₄OH dissociates in a 65°C SC1 bath to form NH₃, H₂O, NH₄⁺ and OH⁻ ions [6]. If the concentration of the H₂O₂ oxidant is insufficient, it is known that exposed silicon will be attacked by OH⁻ ions in solution [7]. The wafers cleaned in O₃ did not experience silicon etching from SC1, hence they weren't as rough.

To further explore Si etching and associated roughness, etch tests were performed with SC1 at 23°C, 35°C, 45°C, and 65°C. Others have shown that roughness induced by SC1 is detectable as an increase in light point defects (LPDs) [8], and Petitdidier et al [6] has illustrated that Si consumption by SC1 correlates directly to LPD number. In this study, wafers were exposed to SC1 for five minutes. SC1 concentration was set to either 100:2:1 or 50:1:1 ($H_2O:H_2O_2:NH_4OH$).

The wafers used in this study were unpatterned 200 mm test wafers with 2000 Å of amorphous silicon (α -Si) over 1000 Å of thermally grown oxide. The α -Si was deposited in an SVG vertical furnace at 560°C. A ThermaWave Optiprobe using spectroscopic ellipsometry was used for all measurements.

103

The average α -Si etch rates for each run are shown in Figure 4. At 65°C, both concentrations of SC1 etched away ~ 7 Å of α -Si per minute. As the temperature of the SC1 was dropped, α -Si loss decreased. At 45°C, only ~3 Å per minute was etched, and at 23°C the etch rates were approximately 1 Å per minute. There did not appear to be a significant change in etch rate if concentration went from 50:1:1 to 100:2:1. In the O₃ clean, < 1 Å of α -Si per minute is removed – this α -Si etch rate was the lowest of any of the tested cleans and within the error of the metrology tool.



Figure 4 Amorphous Silicon Etch Rates

The higher etch rates observed at elevated temperatures indicate a bath condition where NH₄OH dissociation permits attack of α -Si. As the temperature dropped, bath conditions became less aggressive, and less α -Si was etched. The attack of silicon occurring with the SC1 clean was sufficient to impact electrical results, and the minimal attack observed in ozonated water may be a key to the superior electrical performance for the O₃ split.

FOLLOW-UP ELECTRICAL TESTING

To confirm that the attack of silicon in SC1 correlates directly with the electrical observations, a follow-up transistor lot was processed. The O_3 clean was compared to various SC1-SC2 sequences. The SC1 was a 100:2:1 mixture at temperatures of 23°C, 35°C, 45°C, or 65°C. A 200 Å HF/HCl etch was used in all sequences.

In this follow-up work, all splits were found to have nearly identical EOT values (ranging between 21.4 and 21.6 A). The O_3 clean once again showed the highest transconductance, but the low temperature 23°C SC1 process was nearly as good (Figure 5). As the temperature of the SC1 increased, Gm dropped. Saturation current results (Figure 6) showed the same relative trends as the Gm data.

104



Figure 7 shows the effective mobility curves that were generated from the NCSU mobility model. The mobility curves show the same trends evident in the transconductance and saturation current data. The O_3 clean process led to higher mobility than the other cleans, while conditions of the SC1 clearly impacted performance of the SC1-SC2 splits. As the temperature of the SC1 process climbs, Si etch rate increases, and the mobility of transistors is degraded.





Table 2 shows the roughness (length*height) and interface scattering values extracted from the NCSU model. The data suggests that the O_3 clean split had the smoothest surface and the smallest amount of interface scattering. The 23°C SC1 process gave values that were comparable to results with ozonated water. As the temperature of the SC1 process became elevated, roughness and interface scattering increased.

105

Table 2 Roughness and Interface Scattering Data from NCSU Model

	Average		
Clean	Roughness (Å ²)	Interface Scattering (#/cm ²)	
HF/HCl - O₃/HCl	26.75 (st dev = 0.37)	2.76E+10 (st dev = 1.93E+09)	
HF/HCl - 100:2:1 23°C SC1	27.84 (st dev = 0.06)	3.10E+10 (st dev = 1.45E+09)	
HF/HCl - 100:2:1 45°C SC1	30.31 (st dev = 0.18)	5.48E+10 (st dev = 3.45E+09)	
HF/HCl - 100:2:1 65°C SC1	33.50 (st dev = 0.08)	8.77E+10 (st dev = 1.73E+09)	

SUMMARY

The use of ozonated water as a replacement for SC1-SC2 can significantly reduce etching of Si and the resultant microroughness that occurs; the magnitude of the impact will be dependent upon the processing conditions in the SC1 bath. In this work, utilization of O_3 instead of SC1-SC2 led to increased transconductance, saturation current and mobility in electrical tests. The addition of HCl to the HF etch portion of a pre-gate clean was also found to reduce surface roughness and interface scattering on transistor wafers. Replacement of an HF – SC1 – SC2 sequence with an HF/HCl – O_3 /HCl sequence may be advantageous as devices scale to 90nm and below.

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EFFECT OF RIE SEQUENCE AND POST-RIE SURFACE PROCESSING ON THE RELIABILITY OF GATE OXIDE IN A TRENCH

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In this work the effect of post-RIE silicon-surface treatments on the reliability of gate oxide in a trench is investigated. It is shown that the outcome of the etch sequence used to delineate the trench (i.e. main etch) to a large extend determines what type of surface conditioning etch (i.e. soft etch) should be used prior to gate oxidation. The results obtained demonstrate that the resistance of gate oxide in the trench to electric field stress is degraded as compared to flat MOS gate structures, but can be improved using adequate soft etch techniques. The CF₄/Ar soft etch following the Cl₂-based main etch is shown to be the most effective technique. However, there was no effective soft etch observed following SF₆-based main etch.

INTRODUCTION

Power MOSFETs (Metal-Oxide-Semiconductor Field Effect Transistors) devices are designed to handle high current and high voltage switching and rectifying applications. UMOSFET, or U–shaped Trench MOSFET, devices are tailored specifically to lower on-resistance and gate charge, which are the key discrete device parameters. In the Trench MOSFET manufacturing process, the greatest impact on the manufacturing yield and device performance is the extent of surface damage incurred during reactive ion etching (RIE) of the trench and the effectiveness of post-RIE/pre-gate oxidation surface treatments. The goal of this study was to explore the effect of last step in RIE sequences and different post-RIE surface treatments on the integrity of gate oxide thermally grown in a trench. In previous studies it has been shown that without these additional steps high quality gate oxide cannot be formed in the trench [1]. These steps must be specific to trench processing as distribution of breakdown events in the gate oxide on the flat surface despite of the fact that both surfaces were processed and then oxidized simultaneously (Fig. 1).

In this study, the effectiveness of the surface recovery process after trench definition by RIE is investigated. Two different approaches to post-RIE surface re-conditioning are explored. The first involves an additional step ("soft etch") in the trench etch sequence

Electrochemical Society Proceedings Volume 2003-26

applied *in-situ* following "main etch". In the second approach "main etch" is followed *ex-situ* with either slight etching of Si surface in a trench using UV/Cl_2 exposure, or with sacrificial oxidation followed with wet strip of sacrificial oxide. Electrical integrity of gate oxides thermally grown on such prepared surface is then characterized using standard MOS measurements.



Fig. 1. Breakdown field (E_{bd}) of the oxides grown in the trench and planar capacitors under the exact same conditions.

TRENCH ETCH AND SURFACE CONDITIONING

In trench MOSFET processing, the formation of trenches in Si is accomplished by RIE using a specially configured three part plasma etch sequence. In this study etch was designed to form trenches 1-4 microns deep, with $\sim 88^{\circ}$ degree sidewall profile, and rounded bottoms. Undamaged sidewalls are necessary to avoid leakage current along the trench [2]. The Si trench etch sequence consisted of three components which are: (1) oxide removal, or "break-through", (2) the trench formation etch, or "main etch", and (3) the surface conditioning/recovery etch or "soft etch". The first step of the etch sequence is the breakthrough portion, which is designed to remove native or residual thin oxide without effecting the masking profile. In this experiment the breakthrough etch was kept consistent utilizing a Cl₂-based chemistry and was not an essential part of the study. However, the main and soft etches were varied and are key parts of this study. The properties and condition of each are detailed below.

Main Etch

In Fig. 2, SEM photos depict the profiles typically obtained using the two main etch chemistries outlined in this study, specifically SF₆-based and Cl₂-based. In this study the Cl₂-based chemistry typically included HBr and the SF₆-based chemistry included O₂. Each chemistry has specific trademarks including degree of anisotropy, sidewall profile, etch rate, volatility, and ease of removal of etch byproducts. The SF₆-based chemistry as seen in Fig. 2 gives a ~89° sloped profile with rounding of the trench bottom at the transition from the trench sidewall. This chemistry provides a fast Si etch rate [3] and ease of etch byproduct removal [3]. It is known that pure SF₆ chemistry has poor selectivity over SiO₂ [4]. However, in this study the SF₆-based chemistry is used at low pressure and with the addition of O₂, resulting in good etch selectivity over SiO₂. The

Electrochemical Society Proceedings Volume 2003-26

 SF_6 main etch chemistry tends to produce rougher and probably more damaged trench sidewalls than the Cl_2 -based main etch chemistry [4]. In contrast, the Cl_2 -based chemistry, as seen in Fig. 2, gives a more tapered sidewall profile and a smoother Si surface at the trench sidewall and trench bottom. The drawbacks of the Cl_2 -based chemistry are less rounding of the trench bottom, comparatively lower selectivity over oxide, and slower Si etch rate [3].



Figure 2. (a) SF_6/O_2 Etch Profile



(b) Cl₂/HBr Etch Profile

Surface Conditioning Etch - "Soft Etch"

The final step in the etch sequence is designed to recondition or recover the surface in order to form a thin reliable gate oxide. There are a variety of post-RIE surface conditioning techniques that are used in an attempt to chemically or physically alter the trench sidewall and bottom surface. The surface conditioning can be carried out either *in-situ* following main etch or *ex-situ* of the etch chamber. In this study, the chemistries chosen for the *in-situ* soft etch tests were: Cl_2 , CF_4/O_2 , and CF_4/Ar . There was also a cell of the SF_6 main etch chemistry that was processed with an *ex-situ* soft etch treatment using UV/Cl₂. The CF_4/O_2 soft etch was used in conjunction with the Cl_2 -based main etch because there is a halide-polymer produced during the main etch [3]. Therefore, the O_2 in the CF_4 soft etch enhances the effectiveness and removal rate of the halide-polymer layer [3]. The O_2 chemically changes the sidewall polymer enabling fluorine to etch Si from the damaged sidewall surface.

The CF₄/Ar was investigated in combination with the Cl₂-based main etch because it removes damaged Si by both chemical etching with the fluorine and by ion bombardment with argon [5]. The ion bombardment component may be needed because of the increased amount of sidewall polymer produced from the Cl₂-based main etch as well as inadequate volatility of soft etch byproducts [3,5]. The SF₆-based main etch produces a sulfur-based polymer that is easily removed using a Cl₂-based soft etch. The Cl₂-based soft etch chemistry provides a chemical ambient known to readily etch Si, thereby removing the damaged Si from the trench surfaces [3].

The UV/Cl₂ ex-situ gas phase cleaning was done in a reduced pressure anhydrous HF (AHF)/alcoholic solvent to etch chemical oxide and "slightly" etch silicon. The

Electrochemical Society Proceedings Volume 2003-26

operational sequence, without breaking the vacuum, was $UV/O_2 + AHF/methanol + UV/Cl_2$. The UV/O_2 was used to remove polymer, AHF/methanol to remove chemical oxide and the UV/Cl_2 as a "soft etch" of silicon [6].

Sacrificial Oxidation

The damage from RIE can extend several angstroms into the sidewall and trench bottom [5]. This type of damage is well known to affect the electrical behavior of subsequently grown oxides. Figure 3 indicates that sacrificial oxidation improves the breakdown characteristics of oxides grown on the surface of an etched wafer. The main purpose of sacrificial oxide is Si damage removal. In addition, the growth and removal of the sacrificial oxide can round any sharp or concave corners at the bottom of the trench, as well as sharp convex corners at the trench opening [2]. In this study, sacrificial oxidation was not a completely viable solution because of the relatively large amount of Si removed by sacrificial oxidation resulting in the distortion of the trench geometry. Still, because of the benefits noted in Fig. 3 and for the sake of completeness of this investigation, sacrificial oxidation was carried out on all samples unless noted. The sacrificial oxide was nominally 30 nm, which removes ~ 15 nm of silicon.



with and without sacrificial oxidation.

EXPERIMENTAL PROCEDURE

In this study N-type, <100>, 1-10 ohm-cm, 200mm silicon substrates were used. The capacitors were formed by trench patterning into a low temperature oxide (LTO) hard mask and subsequent trench etching into the Si substrate. The trench etch and soft etch splits are detailed above. The UV/Cl₂ *ex-situ* gas phase cleaning was carried out in a commercial cluster tool (Primaxx 2F) at either 50°C or 150°C. Subsequently, unless otherwise noted, a 30nm sacrificial oxidation was carried out followed by a dilute HF etch to remove both the LTO and sacrificial oxide. The wafers were cleaned and then thermally oxidized to form a gate oxide. The resulting gate oxide thickness was nominally 16nm, which is required for power UMOSFETS designed for lower voltage

Electrochemical Society Proceedings Volume 2003-26

discrete applications. The gate contact to both the trench and planar capacitors was made using *in-situ* phosphorus doped poly-silicon and aluminum metal. A Scanning Electron Microscope (SEM) was used to study the cross sections of the trench capacitors.

Electrical Test Structure and Methodology

Figure 4 shows a schematic cross-section of poly-silicon gate planar and trench MOS capacitors used in this study. Test structure in this figure enables measurement of electrical characteristics of the oxide grown simultaneously in a trench as well as on flat surface that was not exposed to RIE. The trench and planar capacitors are electrically isolated by design and tested independently.



Fig. 4. A cross-section of the test structure which includes trench and planar MOS capacitors.

The gate oxide integrity in both the trench and planar capacitor structures was characterized using field-to-breakdown (E_{bd}) and charge-to-breakdown (Q_{bd}) evaluation. They were determined using a Bounded J-ramp (BJR) tests, were J is current density. The current was applied by Keithley 220 Current Source Meter and increased from 1nA with 10 steps/decade and 1 sec/step. After current level reaches 1mA, constant current 1mA was forced until breakdown. The voltage across MOS capacitor was monitored by Keithley 617 Electrometer, and the breakdown was identified when the voltage value decreases 10% or more, i.e., $V_{step i} / V_{step [i-1]} \leq 0.9$. Note that the gate oxide breakdown could occur before or after the applied current reach 1mA, and the measurement was terminated when breakdown was identified and recorded. A minimum of fifty samples were measured at both positive and negative bias. Q_{bd} (C/cm²) was calculated by

$$Q_{bd} = \frac{\sum_{k=1}^{n} I_k \cdot \Delta t}{A}$$
[1]

where A active area, I_k the applied current of step k, and Δt time interval. Since breakdown voltage was also recorded the E_{bd} (MV/cm) can be calculated by

$$E_{bd} = \frac{V_{bd}}{t_{ar}}$$
[2]

where t_{ox} is gate oxide thickness. In some instances, standard constant current stress methodology was used to verify Q_{bd} (C/cm²) measurements especially in the case of UV/Cl₂ ex-situ soft etch test.

Electrochemical Society Proceedings Volume 2003-26

RESULTS AND DISCUSSION

Cl/HBr-Based Main Etch + In-situ Soft etch

In fig. 5 the results are shown of the CF4-based soft etch tests that were run in conjunction with the Cl_2 main etch. The results indicate that the soft etch, post Cl_2 main etch, does positively affect the surface recovery. The CF4 in the gas mixture and etch conditions (i.e. pressure and power) provides an isotropic component under which the CF_4 dissociates to form free F radicals to attack the sidewall polymer [3]. The results also show the enhanced performance of using Ar verses O2. The enhancement is noted by increased values of Ebd and Qbd. In addition, there is a significant defect tail seen in the O_2 data for both distributions, which indicates less effective surface damage removal verses argon. The physical nature of the Ar incorporated into the soft etch shows itself to be more effective than the chemical nature of the O₂ incorporated into the soft etch. Argon also provides ion bombardment to aid in physical removal of sidewall polymer as well as removal of Si damage from the exposed surface once the polymer is removed. Whereas, the O2 in the CF4-based soft etch enhances the chemical removal rate of the sidewall polymer by forming a removal volatile byproduct. Argon is inert it does not chemically react with Si; however O₂ has a high affinity for Si and readily reacts. Therefore, Ar provides a faster, more physical and isotropic etch, resulting in a more rounded bottom. The bottom rounding helps give improved electrical characteristics [1].



Figure 5. Comparison of Cl_2 /HBr main etch and CF_4 /Ar soft etch vs. Cl_2 /HBr main etch and CF_4/O_2 soft etch through (a) Breakdown field (b) Charge to breakdown.

<u>SF₆-Based Main Etch + In-situ Soft etch</u>

Fig.6 shows that the SF₆ main etch causes damage to the wafer surface and the Cl₂ soft etch following the SF₆ main etch does not improve the Q_{bd} and E_{bd} characteristics. Using an SF₆-based chemistry; more free radicals are introduced into the gas mixture as compared to Cl₂-based chemistry. Also, an anisotropic etch is obtained through the formation of polymer acting as a sidewall etch inhibitor. However, surface roughness is increased. Previous AFM studies on planar surfaces etched using SF₆-based chemistry showed as much as 10 times more surface roughness than Cl₂-based chemistry [4]. While no AFM studies have been carried out on etched trench sidewalls, it is reasonable to expect similar surface roughness variations between the etch chemistries on the trench sidewall. This is provided that the etch conditions and amount of exposed Si are

113

nominally the same. Furthermore, the Si substrates used were rotated 45° off the notch, which put the trench sidewall on the same orientation, <100>, as the top surface. Therefore, if SF₆-based chemistry is used as the main etch, a different chemistry is needed to remove the surface roughness produced by it. Chlorine, with its less aggressive Si attack should be ideal for this. Moreover, the bottom rounding formed by the SF₆ main etch is not severely affected by the anisotropic nature of the Cl₂ soft etch, typically resulting in improved oxide integrity [1]. However, in this study it is clear that the overall etch damage removal was inadequate. An alternative approach to the use of Cl₂ as a soft etch after the SF₆ main etch was investigated due to the amount of damage from the main etch.



Figure 6. Comparison of $SF6/O_2$ main etch and no soft etch vs. SF_6/O_2 main etch and Cl_2 soft etch through (a) Breakdown field (b) Charge to breakdown.

SF6-Based Main Etch Chemistry & Ex-situ UV/Cl2 Surface Conditioning

114

In an alternative approach to soft etching post- SF_6 main etch, a UV/Cl₂ process was applied ex-situ of the main etch chamber. The test was done in contrast to sacrificial oxidation at either 50°C or 150°C. The results in fig. 7 indicate that 50°C, UV/Cl₂ treated capacitors have better breakdown strength than 150°C, UV/Cl₂ treated capacitors. However, the capacitors with sacrificial oxide treatment and no soft etch, show better breakdown strength [0.5-1 MV/cm] as compared to any UV/Cl₂ treated capacitor. This indicates that the Cl₂ soft etch in this approach was inadequately applied. Previous studies have shown effective Si removal using UV/Cl₂ process, typically less than ~5nm [6]. Therefore, the unfavorable results are likely an indication that the etch damage was not completely removed. Further evidence of inadequate removal of damage after both the sacrificial oxidation and the UV/Cl₂ process is confirmed by the inability to obtain Qbd measurements on trench capacitors. In the Qbd measurements, the leakage current was too large to complete any tests. The reasonable E_{bd} values coupled with the lack of trench Qbd values confirms that surface roughness was not removed. Furthermore, the planar capacitors, which were not given any etch treatment, show an overlap in their breakdown strength with negligible spread in values, indicating that the effects seen in the trench capacitors are indeed due to the etch treatment. These results mimic those of the in-situ Cl_2 soft etch findings. The overall notion is that Cl_2 may be an adequate chemistry, but more damage removal is needed with either method of soft etching.



Figure 7. Comparison of SF₆ main etch and soft etches $-UV/Cl_2$ [150°C] vs. UV/Cl_2 [50°C] vs. sacrificial oxidation through breakdown field.

CONCLUSIONS

In this study, the effect of post-RIE silicon-surface treatments on the reliability of gate oxide in a trench was investigated. There are three parts to the etch sequence used to form the trench which are the break-through, main, and soft etch. The "main etch" leaves sidewalls and the bottom of the trench severely damaged, and hence, must be followed by an additional surface conditioning treatment. The CF₄/Ar soft etch following the Cl₂-based main etch is shown to be the most effective in this regard. Both the *in-situ* Cl₂-based and the *ex-situ* UV/Cl₂ soft etch processes show inadequate removal of the damage caused by SF₆ main etch. This observation once again leads to the conclusion that optimization of the main etch is a key element in developing successful U-trench MOSFET technology.

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MINIMIZING OXIDE LOSS IN IMMERSION SC1 PROCESS

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Particle removal efficiency is studied as a function of several different SC1/megasonics parameters while trying to maintain oxide loss at less than 1Å. It is found that high particle removal efficiency can be maintained down to oxide loss levels of 3Å in a spray acid tool. Below this level of oxide loss particle removal efficiency is greatly reduced for both spray and immersion tools. There is also a dependence on dissolved gas where high and low levels of dissolved gas cause a reduction of particle removal, while an intermediate level, corresponding to about 450 ppb of dissolved oxygen gives optimal particle removal. With tank modifications, megasonics energy can be used to remove particles with an oxide loss of 1Å and without damaging 60nm wide polysilicon lines with an aspect ratio of over 3.0.

INTRODUCTION

In current integrated circuit manufacturing processes, the gate electrode and surrounding surfaces are subject to increasing cycles of implant mask ashing and cleaning. This is being driven by the desire to have transistors with several different threshold voltages on the same chip. Since each different type of transistor needs several different implants, there can be up to 15 implant masks, each with subsequent ashing and cleaning, after the gate electrode has been formed. With the simultaneous decrease of the gate electrode width, this is posing a challenge for post-ash cleaning, which is targeted at removing ashing residues as well as particle contaminants. Traditional megasonics is not currently used at this stage in device manufacturing because it causes damage to gate structures narrower than 100nm. Consequently, increased material removal (etching) is required in order to achieve sufficient particle removal efficiency. However, the increasing number of cleaning steps is forcing a reduction in the allowable amount of material removed. The sequence of ashing and cleaning also causes the silicon surface to be oxidized and then etched away. These issues are illustrated in Figure 1, which shows the cross-section of a 90nm node transistor indicating areas of concern for material loss. The challenge for cleaning devices currently in production is to achieve sufficient particle removal efficiency while controlling the amount of material loss and avoiding damage to the gate electrode. Current manufacturing processes are requiring less than 1Å of thermal oxide loss per cleaning cycle with less than 0.5Å being specified in just a few years.

The ammonium hydroxide / hydrogen peroxide / water solution, also known as SC1, is the predominant chemistry for achieving particle removal in front end cleaning. When sensitive structures are not present, megasonics energy is applied to assist in particle removal. Without megasonics energy, surface etching is required to detach particles. There have been many studies of the SC1 chemistry over the 30 years since it was first introduced by Kern and Poutinen [1]. Some studies have focused on the surface effects of SC1, measuring the etching rate of silicon and silicon dioxide as well as surface

roughening [2-5]. Other studies have focused on particle removal as a function of SC1 parameters [6-7] without studying the influence of material loss. Meuris and co-workers found that a minimum removal of 20Å of oxide was required to achieve more than 95% particle removal at >0.2 microns while immersing wafers in dilute HF without megasonics energy [8]. Christenson and co-workers found that removal of 15-20Å of oxide was required to achieve 99% particle removal at >0.15 microns while spray wafers with SC1 solution in a spray acid tool [9-10]. More recent studies by Meuris et al. [11] and Vos et al. [12] have also proposed that a minimum removal of 30Å of oxide is required to achieve sufficient particle removal. This level of oxide removal is clearly not acceptable for post-ash cleaning with integrated circuits now in production.



The focus of this study is to investigate the effect of SC1 and megasonics tank parameters on particle removal efficiency while maintaining very low oxide removal. The goal is to achieve high particle removal efficiency while avoiding damage to the gate electrode.

EXPERIMENTAL

A four-variable, three-level Box-Behnken experimental design was used for the main study. Megasonics power (400W, 1200W, 2000W), SC1 temperature (25°C, 40°C, 55°C), SC1 dilution (1:1:50, 1:1:125, 1:1:200), and solution degassing (0, 10, 20 inches Hg vacuum) were the controlled variables. Particle removal efficiency was measured for silicon nitride particles which were wet deposited on bare-300mm wafers (with SC1 chemical oxide present), allowed to "age" for 24 hours, and analyzed using a KLA-Tencor SP1 for nominal sizes greater then 90nm. For the particle removal tests, the challenge wafers were processed in full, 52-wafer batches, and were run for 2 minutes for each of the experimental design conditions. For each condition, the SC1 step was

117

followed by 2 cycles of quick dump rinsing and a final surface tension gradient dry. Oxide loss was measured separately on thermal oxide wafers for each combination of SC1 temperature and dilution in the experimental design. A flat-bottom quartz tank was used with a 4-quadrant megasonics transducer attached to the bottom. Preliminary data was also collected without megasonics energy and also with SC1 solutions dispensed in a spray acid tool to gain a better understanding of the etching effect, alone. Also, a final test of tank modifications was run to demonstrate elimination of megasonics damage to sensitive polysilicon structures.

RESULTS AND DISCUSSION

The preliminary results without megasonics and also with a spray acid tool are shown in Figure 2. For the spray acid tool, particle removal efficiency stayed high for oxide losses down to 3Å. Below 3Å of oxide loss in the spray tool, particle removal efficiency drops of significantly, down to about 30% for a 1Å oxide loss. For the immersion tank without megasonics, removal efficiency falls off at a higher oxide loss level. At 3Å oxide loss, the removal efficiency in the immersion tank without megasonics is only 60%. This difference between the spray tool and the immersion tank without megasonics indicates the influence of flow dynamics on particle removal. In the spray tool, centrifugal forces are used to propel chemical and water off the wafer surface at high velocity reducing the distance which particles much diffuse away from the surface and enhancing their removal. Also, it should be noted that the fall off in particle removal efficiency for these 90nm particle tests occurs at a much lower oxide loss than that indicated by previous studies which measured removal efficiency at >200nm [8] and at >150nm [9-10]. One possible explanation for this difference is that smaller particles might be more easily undercut, requiring less oxide removal, than larger particles.



The results of the designed experiment indicate that particle removal efficiency is a strong function of megasonics power and of SC1 solution temperature, increasing with both parameters, and only a weak function of SC1 dilution. The dependence on megasonics power is as expected. The dependence on temperature is most likely linked to the increase in oxide loss with the increase in temperature. Figure 3 shows the thermal oxide loss dependence on both temperature and SC1 dilution. It is evident that SC1 dilution over this range has a very weak effect on oxide loss and thus on particle removal.



The dependence of particle removal efficiency on dissolved gas is very interesting. As the dilution water is degassed, the particle removal efficiency initially rises as shown in Figure 4. However, at a certain point, corresponding to a dissolved oxygen level of about 450 ppb, the particle removal efficiency falls sharply with further decreases in dissolved gas level. One possible explanation is that at high dissolved gas levels, most of the megasonics energy is used to create bubbles that collapse near the bottom of the tank. As the dissolved gas levels are reduced more energy is transmitted to the top of the tank and the entire surface of the wafer is cleaned. However, if the dissolved gas levels are reduced too much, cavitation bubbles will no longer form and the megasonics energy will be simply transmitted to the top of the tank without dislodging any particles.

Figure 5 shows the dependence of particle removal efficiency on oxide loss at 1200W and at two different dissolved gas levels. The particle removal efficiency decreases with lower oxide loss even with megasonics energy applied to the wafer.

Electrochemical Society Proceedings Volume 2003-26





Electrochemical Society Proceedings Volume 2003-26

The final question is whether megasonics can be applied at these conditions to achieve particle removal without damaging sensitive structures. Tests were carried out using dense arrays of polysilicon lines which were 60nm in width and 220nm in height. While a traditional megasonics configuration caused significant damage to these lines, a modified megasonics configuration that was able to achieve 80% removal of 90nm silicon nitride particles with a 1Å oxide loss, did not cause any observable polysilicon line damage. Additional work is required to demonstrate efficient, non-damaging particle removal on actual production integrated circuits with oxide removal of 0.5Å.

CONCLUSIONS

Several aspects of particle removal in low oxide etching SC1 solutions were studied. By comparing the removal efficiency in a spray tool with that of an immersion tank without megasonics, the importance of fluid dynamics becomes evident. It was also shown that with oxide loss of less than 3Å megasonics energy is required to efficiently remove particles. Finally, particle removal can be achieved with low oxide etch and without damage to sensitive structures through optimization of multiple parameters including megasonics energy distribution and dissolved gas content.

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PERFORMANCE OF AN ADVANCED FRONT-END-OF LINE CLEAN COMPARED TO THE PROCESS OF RECORD CLEAN IN A MANUFACTURING ENVIRONMENT

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ABSTRACT

With the critical device dimensions continuing to shrink below 100 nm, wafer surface preparation prior to gate oxidation has become more critical for high device yields. [1,2]. Numerous papers have established that an Advanced Front End of the Line clean (AFEOL) is capable of providing improved particle and metallic results [1-3], but still the process of record clean (POR) which is typically based on an RCA type process still dominates most process lines today. This is based largely on the large inertia it takes to migrate to a new clean in established process lines. This paper will describe the AFEOL clean and POR clean and characterize the differences between them seen by in-line monitor wafers and short loop GOI device testing. This work was done at the Honeywell Solid State Electronics Center as part of a production yield improvement program through advanced pre-diffusion wafer cleaning.

EXPERIMENTAL

The process of record clean (POR) was a modified RCA clean. A sacrificial PAD oxide strip was done in 10:1 HF followed by an SC1 clean utilizing megasonics. The clean next employs a 200:1HF dip for 15 seconds to strip part of the native oxide but not all, leaving the surface hydrophilic. This has the effect of greatly reducing the metallic signature seen by photoconductive decay lifetime measurements in wafers not partially etched. The POR clean continues with an SC2 clean followed by a spin rinse dry. The AFEOL clean, a layout of which is shown in figure 1, starts with an ozonated recirculated rinse in >25 ppm ozone followed by a 20:1:0.2 H₂O:HF:HCl mixture to strip sacrificial oxide. The HCl is added to the HF to prevent metal induced pitting. A rinse in >8ppm ozonated water reoxidizes the surface prior to a dilute SC1 preventing any pitting (LPD generation) from ammonia attack on the silicon surface. . The dilute SC1 was followed by a 1000:1 HF to remove the native oxide and metals from the SC1 process while controlling oxide loss. This was in turn rinsed in one pass ozonated water with >8 ppm ozone bubble free to grow a uniform metallically clean oxide. A Surface Tension Gradient type dryer was employed for drying that was spiked with 1000:1 HCl to prevent metal contamination being adsorbed from DI water on the native oxide. This sequence was the

Electrochemical Society Proceedings Volume 2003-26

basic one for pre-gate cleaning, but several other chemical sequences were used that were variations of this basic layout. The system was capable of random access to each tank so other cleaning sequences were simply a matter of rewriting recipes. Three recipes will be discussed in the results section to follow.

RESULTS AND DISCUSSION

Several variations of the AFEOL clean were implemented. One variation used no HF to minimize oxide loss. This consisted of a recirculated ozonated water tank with >25 ppm dissolved ozone followed by a dilute SC1 megasonic process. The dry consisted of HCl at a concentration of 1000:1 injected into a low consumption IPA dryer. Figure 2 is the trend chart over a 20 day period showing the results of 150mm float zone test wafers run through the clean and measured on a Tencor SP1 measuring "true adders" at 0.1um. The float zone material was chosen to minimize the effects of crystal originated particles (COP's) or oxygen vacancies on LPD counts. Before this strategy was employed typical CZ silicon test material showed significant variability in LPD counts and suspicion was raised that this was not the process, but the quality of test material measured at this small LPD size and the resulting "etching out of COP's" by SC1. This proved to be true since float zone material has no oxygen and the resulting LPD counts were low as shown in Figure 2. True adders were less than 7 particles measured at 0.1 μ m for all runs.

Table 1: Process of Record Clean and AFEOL Cleans Description

- Process of Record Clean:
 - SC1 + QDR + DHF(200:1 @15 sec) + Cascade Rinse+SC2 + QDR + Spin/Rinse Dry
- AFEOL Cleans:

o Low Oxide Loss

- DIO3 (>25 ppm) + SC1 + QDR + 1000:1 HCl Injected into IPA dryer

o Pre-Gate

—DIO3 (>25 ppm) + 20:1:0.2 HF/HCl + >8 ppm O3 Rinse + DIO3 (>25 ppm) + SC1 + QDR + 1000:1 HF + >8 ppm O3 Rinse + 1000 :1 HCl Injected into IPA Dryer

HF Last DIO3 (>25 ppm) + SC1 + QDR + 1000:1 HF + Rinse + 1000:1 HCl Injected into IPA Dryer

A second variation of the AFEOL clean, used for pre-gate cleaning had a 20:1:0.2 HF/HCl added for sacrificial oxide removal after the initial DIO3 process. An ozonated rinse process was used after the oxide etch to regrow a native oxide. A recirculated DIO3 was then done next followed by a dilute megasonic SC1 process and QDR rinse. A 1000:1 HF process was used to remove the native oxide (and metals) followed by a once through ozonated rinse at >8 ppm bubble free ozone to regrow a very clean oxide. The dry was

the same 1000:1 HCl injected into the low consumption IPA dryer as previously described. The control chart for this clean is shown in Figure 3. All daily particle checks on float zone material were less than 7 true adders at 0.1um except for 2 points which were at 17, and 14. It was noticed that for these runs bubbles were in the final ozonated rinse tank. Once adjustments were made to remove these bubbles the particles decreased. A third variation of the AFEOL clean was used that had the ozone turned off in the final rinse tank. This version yielded a hydrogen-terminated surface. The control chart for this clean is shown in figure 4. The values achieved are below the equivalent POR clean by a factor of more than five.

Several electrical parameters were considered for the comparison between the two cleans. A sample listing is included in Table 2. As shown in Table 2 the cleaning results of the AFEOL clean are far better than those obtained from the POR. Utilizing the Microwave Photoconductive Decay (μ -PCD) measurement technique, the "Furnace #1" minority carrier lifetime results were comparable and the Fe contamination results were 50% lower on monitor wafers after the furnace processing. Significantly raised lifetime and lowered iron concentration results were obtained for both "Furnace #2" and "Furnace #3" processing. Thus it is clear that the AFEOL clean is superior in providing a lower equivalent Fe content and an improved minority carrier lifetime.

Historical data on the POR for etch uniformity is not available since it did not pass the uniformity criterion. The etch uniformity obtained for the AFEOL met the integration criterion of 1% at 1 sigma for 100-200 A of SiO₂ film thickness. Figures 5 & 6 are of the run to run etch rate consistency of this system for the 450A etch and the thin etch of SiO₂, BPSG and TEOS films respectively. Reproducibility of the etch rate of this system is very good. A control system, based on the real time measurement of the HF concentration, was used for the thin oxide etch. The sensor used is an electrodeless conductivity sensor integrated into the recirculation loop. This system allows the chemistry to be batched to conductivity which has been found to be more accurate than volumetric blending. This control system could not be used on the bath using 20:1:0.2 water:HF :HCl because of the tri mixture. There is no way to tell the HF concentration from the HCL concentration. Figure 7 shows the etch rate and its stability over time of SiO₂, TEOS, and BPSG films in the SC1 chemistry. This consistency is required to predict the oxide loss for the SOI process.

Figure 8 is a measurement of the iron (Fe) levels in the wafer measured by Microwave Photoconductive decay on a float zone wafer. The minimum is 1E8 atoms/cm³ for 30% of the 3000 measurements points on a 150 mm wafer. The average value is 2.6E8 atoms/cm³. These levels are not achievable for standard RCA cleans.

Table 2: Test results of AFEOL versus FOR Cleans					
Parameter	POR	AFEOL	Results*		
Furnace #1 Lifetime 80%, µs	1698	1577	\uparrow		
Furnace #1 Fe 20%, atoms/cm ²	7.7E9	2.3E9	$\uparrow \uparrow \uparrow$		
Furnace #2 Lifetime 80%, µs	2326	2625	↑ ↑		
Furnace #2 Fe 20%, atoms/cm ²	2.4E9	2.0E9	<u>↑</u> ↑		
Furnace #3 Lifetime 80%, µs	390	788	↑↑↑		
Furnace #3 20%, atoms/cm ²	4.9E10	1E8	<u>↑</u> ↑↑		
True added Particles, 0.15 µm	32	1.3	$\uparrow \uparrow \uparrow$		
Removal Efficiency, %	95	97+	↑↑		
Surface Metal Contamination	NA	Pass	↑↑↑		
Oxide Etch Uniformity	NA	Pass	$\uparrow\uparrow\uparrow$		

Table 2: Test results of AFEOL versus POR Cleans

↑ Designates AFEOL clean outperforms POR clean.

The table represents lifetime data as monitored by the Microwave Photoconductive decay (u-PCD) technique. The 80% lifetime number (μ sec) means that 80% of the measured points (3000/150mm wafer) are above this value. The 20% iron number (atoms/cm²) means that 20% of the measured points have iron concentrations above this value.

CONCLUSIONS

A case study was conducted to compare an existing clean (POR) with a new clean (AFEOL) in an SOI manufacturing environment. The results show that the AFEOL clean outperformed the POR in almost every parameter that was considered for the study. The results are mainly due the very low defect (particles and metals) density obtained in the AFEOL. The quality and stability of the Si/SiO₂ interface formed during the AFEOL clean was remarkably better than that obtained in the POR cleans.

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Figure 1: GAMA AFEOL Configuration



Figure 2: Trend Chart for DIO3 + SC1 + HCl Injected into Dryer True Particles Added Performance @0.1µm







Figure 5: Control Chart on the oxide etch rate in 20:1:0.2 DIW: HF: HCl solution.



Figure 4: Trend Chart for DIO3 + SC1 + DHF + HCl Injected IPA Dry- HF Last



Figure 6: Control Chart on the oxide etch rate in 1000:1 DHF solution.



Figure 7: Control chart of the etch rate for various films in the SC1 solution.



Figure 8: Typical Lifetime for AFEOL Clean Measured using Float Zone Silicon

THE MECHANISM OF POLY-SI ETCHING DURING POLY/W GATE CLEANING BY FLUORINE BASED CLEANING SOLUTION

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ABSTRACT

When W/WN/poly gate stack was etched, an oxide-like polymer was formed on the sidewall and the bottom. To remove the polymer, fluoride based chemicals had been used because it had oxide etch ability. These were excellent to clean the polymer, however, these solutions also etched poly silicon resulting in the undercut of gate poly-Si. It had been believed that poly-Si showed very low etch rate in fluoride based chemicals but there was a considerable change of etch characteristic according to the crystallographic change by heat treatment. The more interesting result is that the etch rate of poly-Si highly depend on the types and the concentration of dopant. From these results, we could explain the severe gate poly-Si undercut was due to the increased etch rate of gate poly-Si, which was implanted by phosphorous, by heat treatment effect during mask SiN deposition process.

INTRODUCTION

As device shrinks, it becomes necessary to introduce a poly/metal gate structure that has lower electrical resistance than poly/metal silicide gate. In these days, poly/W gate is widely studied and used as a DRAM device to reduce gate stack height and RC delay. Even though these benefit, there are some issues to integrate poly/W gate. When poly/W gate stack is etched, an oxide-like polymer is formed on the sidewall and the bottom [1]. This is more difficult to remove because the selection of cleaning chemical is very limited due to the corrosion of W. Conventional cleaning solution such as SC1 and SPM cannot be applicable to poly/W gate cleaning. To remove this polymer, fluoride based solutions can be used as cleaning solution due to its oxide etch ability. In fact, fluoride based chemicals are excellent to remove the oxide-like polymer. However, as shown in figure 1, these solutions also etch poly-Si resulting in the unwanted gate profile and degradation of electrical characteristics, especially decreasing threshold voltage. Up until now, it has been believed that poly-Si shows very low etch rate in fluoride based chemical. However, severe poly-Si undercut happened after gate etch cleaning in fluoride based solution.

EXPERIMENTAL

The schematic diagram of Poly/W gate pattern that used in this study is shown in figure 2. HBr/O2 gas was used to etch poly-Si to increase the etch selectivity to gate oxide. To measure the etch rate, phosphorous doped poly-Si 1000 Å which used as a gate poly-Si and undoped poly-Si 2000 Å was deposited on a thermal oxide 1000Å. To measure the dependence of dopant types and concentration, boron and phosphorous was implanted on undoped poly-Si by 5E14/cm², 5E15/cm² which was annealed at 1000 $^{\circ}_{\rm C}$ for 2 minutes by RTP.

Electrochemical Society Proceedings Volume 2003-26



Figure 1. TEM image of poly/W gate damaged by fluorine based solution.

Figure 2. Schematic diagram of poly/

SiN

W/WN

Poly

Sub-Si

RESULTS AND DISCUSSION

Gate Oxide

W gate

1. The aspects of polymer generation and issues of cleaning after poly/W gate etch.

The polymer generated after poly/W gate etch is known as a oxide-like polymer having SiOx structure [1]. To remove this polymer, the cleaning solution should have oxide etch ability. Amine based solution, which have been used as polymer stripper after metal etching could not remove this polymer because it didn't have oxide etch ability. As shown in figure 3 (a), amine based solution could not remove this oxide like polymer and it could be seen the remain polymer between gate stack and capping SiN. On the other hand, fluoride based solutions showed excellent removal efficiency and we could not see a boundary between gate and capping SiN. By using this VSEM(Vertical SEM) image, it could be known that the minimum oxide etch amount to remove this polymer is ~2 Å, ~8 Å for thermal oxide and PE-TEOS, respectively. As shown in figure 4, over 8 and 10 minutes were required to remove this polymer generated on sidewall of gate stack for fluoride based solution A and B, respectively. The polymer also generated on a bottom side which was thicker than sidewall polymer. This could be known from the thickness and etch rate changes of bottom thermal oxide that is called gate oxide. As shown in figure 5, the initial gate oxide thickness was 100Å but this was increased to 152 Å after gate etch. The gate oxide also showed different etching rate in fluoride based solution A and 1000:1 HF as according to the treatment times. The etch amount of gate oxide in solution A for 8 minutes was 25 and 35 Å at the first and second treatment, respectively, which was 12~17 times higher than the etch amount of thermal oxide. Additional treatment in solution A for 5 minutes showed dramatic decrease of etch amount to 4 Å but still higher than that of thermal oxide. After this, the etch amount of gate oxide was \sim 3Å which is similar to thermal oxide. The initial etch amount which had high etching rate was about 60 Å and this was similar to the increased gate oxide thickness after gate etch. From this result, it can be thought that the increase of gate oxide thickness after gate etch was due to the polymer generation on bottom side. That is, it should be needed over 16 minutes treatment in solution A to remove the polymer generated on the bottom side. It took over 16 minutes to remove the polymer which was generated after gate etch but this time was enough to occur poly undercut. But the poly undercut was observed only after 8 minutes treatment in solution A and the undercut was increased as the treatment time was increased.

Electrochemical Society Proceedings Volume 2003-26



Figure 3. SEM image of poly/W gate after treatment in amine based stripper (a), 35_{C} , 20min and fluoride based solution A 35_{C} , 8min (b)





Figure 4. The etch amount of PE-TEOS in solution A, B at 35 $^{\circ}_{\rm C}$ and 1000:1 HF at R. T.

Figure 5. The changes of remain oxide thickness as the continuous solution A and 1000:1 HF treatment.

2. The mechanism of poly-Si undercut

Fluoride based solution A and B are weak acid having \sim pH 4.3. The etch rate of asdepo poly-Si was very low as \sim 0.2, \sim 0.13Å/min in solution A and B, respectively. So it could not be understood that the poly-Si undercut during post etch cleaning in fluoride based solution. At the first time, we thought the poly undercut as galvanic corrosion between W and poly. Some authors reported that crystal defect such as etch pit was observed on poly-Si that contact with noble metal such as Pt by galvanic corrosion [2]. But this hypothesis was proved as untruth experimentally. As shown in figure 6, we made a poly and mask SiN pattern without W and there was also the poly undercut after 10 minutes treatment in solution A.

Secondly, we evaluated the effect of heat treatment on etch rate because it had been thought that the poly-Si would show various etch rate according to its crystallographic aspects. Figure 7 shows the etch amount of phosphorous doped gate poly-Si in fluoride based solution A, and B for 10min at 35 $^{\circ}$ C. As shown in figure 7, the etch amount of asdepo poly-Si was just ~2Å in solution A and ~1.2 Å in solution B. After SC1 and dilute HF treatment in order to remove the native oxide and other contaminated layer on the surface, the etch amount of poly-Si was sill very low. However, after RTA at 950 $^{\circ}$ C for 300 seconds, the etch amount of poly-Si was dramatically increased to 88 Å in solution A and 51 Å in solution B. This result showed that the etch rate of poly-Si could be changed



Figure 6. SEM image of poly/SiN stack after treatment in solution A at $35 \circ$ for 10 minutes.

132



Figure 7. The etch amount of poly-Si in fluorine based solution A and B at $35^{\circ}_{\mathbb{C}}$ for 10 minutes.



Figure 8. The etch amount of poly-Si in solution A for 10 minutes as a function of dopant concentration and type.

by following heat treatment. Actually, the deposition of mask SiN that was high temperature process(over $750 \,^{\circ}$) was followed by the deposition of poly-Si in device integration, so the poly-Si undercut could be explained by the increase of etch rate by heat treatment effect during mask SiN deposition.

The increase of etch rate of poly-Si by heat treatment might be related to the crystallographic change and the electrical change by dopant activation. Figure 8 shows the etch amount of poly-Si in solution A for 10minutes at 35° after RTA process $(1000^{\circ}C, 2minutes)$. As shown in figure 8, the etch amount of undoped poly-Si was approximately 21Å which was over 5 times larger than as-depo amorphous Si. This increase of etch rate may be due to the crystallization of as-depo amorphous Si by RTA. This result indicates that the etch rate can be increased only by the crystallization of amorphous Si. It could be thought that the increase of etch rate by crystallization was due to chemical attack through a grain boundary because it is weak point. The more interesting result was that the etch rate of poly-Si was highly depended on the types and concentration of dopant. As shown in figure 8, in case of boron doped p-type poly-Si, the etch rate was decreased as boron dose amount was increased. The etch amount was decreased from ~7Å to ~1Å as the dose amount is increased from 5E14 to 5E15 atoms/cm². On the other hand, the etch rate of phosphorous doped n-type poly-Si showed opposite trends. Phosphorous doped n-type poly-Si showed 90 times larger etch rate than boron doped p-type poly-Si at the 5E15 atoms/cm² dose amount.
This etch rate difference may be related to the space charge, in other word fixed charge, near the interface of poly-Si and solution. We still cannot explain this result quantitatively, but the qualitative explanation may be possible. In the case of an n-type poly-Si that implanted by phosphorous ion is immersed in fluoride solution, extra electrons will initially move across the interface, reducing O ions in solution [3]. As this takes place, the ionized fixed charges remaining in the poly-Si form the space charge layer having sub m thickness from a surface. The potential difference that results from the formation of this layer compensates the original tendency of electrons to escape from the poly-Si, and the Fermi levels on both sides of the interface become equal. In this case, the fixed charges are P+, so the negative ions such as OH- can easily diffuse to the poly-Si surface. It is well known that the main species etching a silicon is OH ion, so the silicon have a very high etch rate in alkaline solution such as KOH and NH OH but the silicon is very stable in acidic solution. Even though the fluoride based solutions are weak acid of which the pH is ~4.5, it is expected that the concentration of OH ion is high at the interface of n-type poly-Si and solution due to the attractive force of space charge. Because the concentration of space charge is determined by the concentration of dopant the etch rate is increased as the concentration of dopant is increased. On the other hand, in the case of boron doped p-type poly-Si, the space charges are negative boron ions, so it is expected that the concentration of OH ion is very low at the interface because there are repulsive forces between space charges and OH- ions.

From this model, we could explain the higher etch rate of n-type poly-Si than ptype poly-Si, effect of concentration of dopant and the heat treatment effect.

CONCLUSIONS

The etch rate of poly-Si in fluoride base solutions highly depended on the heat treatment, dopant type and concentration. The etch rate was decreased as boron dose amount was increased. The etch amount was decreased from \sim 7Å to \sim 1Å as the dose amount is increased from 5E14 to 5E15 atoms/cm². On the other hand, the etch rate of phosphorous doped n-type poly-Si showed opposite trends. Phosphorous doped n-type poly-Si showed 90 times larger etch rate than boron doped p-type poly-Si at the 5E15 atoms/cm² dose amount. This etch rate difference could be explained by the relationship of space charge and OH- ions in fluoride based solutions. From these results, we could explain the severe gate poly-Si undercut was due to the increased etch rate of gate poly-Si, which was implanted by phosphorous, by heat treatment effect during mask SiN deposition process.

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Electrochemical Society Proceedings Volume 2003-26

Physical and Chemical Methods of Particle Removal

MECHANISMS OF PARTICLE REMOVAL DURING BRUSH SCRUBBER CLEANING

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The article focuses on the mechanisms of particle removal during brush scrubber cleaning for nano-sized slurry particles. The removal of Clariant SiO_2 slurry particles with average size of 34nm from nitride substrates is investigated. To measure such nano-sized particles on wafers, the haze signal is used. After a scrubber clean, the uniformity of the particle radial surface concentration on a wafer is checked. The processing time effect on the particle removal is analysed afterwards. Based on rolling and lifting removal mechanisms, some initial models are developed to describe the particle radial surface concentration after scrubbing. By doing so, the removal mechanisms of scrubbing under varied scrubbing conditions are determined. Finally, some experimental evidences on the particle removal mechanisms are shown in this study.

INTRODUCTION

With shrinking dimensions of the IC structures, the impact of particles upon device yield becomes more and more important. To ensure high device yields, wafer surface contamination and defects must be monitored and controlled at several points in the semiconductor manufacturing process. Brush scrubbers are among the tools used to achieve such control and they have become one of the dominant instruments for wafer cleaning applications nowadays.

A lot of scientists are working in this field, trying to disclose the particle removal mechanisms during brush scrubber cleaning. For example, Philipossian *et al* studied the tribology during the brush scrubber cleaning, focusing on the coefficient of friction by varying the instrumental parameters of scrubbers and implying that the hydrodynamic drag force is a very critical factor on particle removal [1]. By introducing the critical particle Reynolds number, Burdick *et al* set up a model and claimed that rolling is the dominant particle removal mechanism during brush scrubbing and it is a must to have brush/particle contact in order to remove particles [2, 3]. Focusing on the adhesion and removal forces of a particle on a substrate during brush scrubbing, Busnaina *et al* found having full contact between brush and particle is a must to lift or roll particles smaller

Electrochemical Society Proceedings Volume 2003-26

than $0.1 \mu m$ off a substrate [4]. However, up till now, the particle removal mechanisms of brush scrubber cleaning are far from well understood, especially because limited experimental data to back up all those theoretical models are available.

The forces that a particle receives during a brush scrubber clean are schematically depicted in Figure 1. Basically, the particle removal mechanisms can be categorised into three: lifting, sliding and rolling [5].

1) Lifting mechanism: particles will be removed from the surface if the brush-particle adhesion force F_A overcomes particle-wafer

adhesion force F_a and the external brush load F_b .

$$F_A \ge F_a + F_b \tag{Equ. 1}$$

2) Sliding mechanism: particles can slide off a substrate if the sum of the hydrodynamic drag force of the fluid F_D and the friction force particle/brush F_F is bigger than the friction force particle/substrate F_f .

$$F_D + F_F \ge F_f = \kappa (F_a + F_b - F_A) \quad (\text{Equ. 2})$$

with κ the friction coefficient particle/substrate.



Figure 1: Schematic description of the forces a particle receives during brushing.

3) Rolling mechanism: if the torque balance of a particle during scrubber cleaning is considered, the particle can be rolled off the wafer if the following equation works [6, 7]:

$$1.4F_F + F_D \ge \frac{a}{1.4R}(F_a + F_b - F_A)$$
(Equ. 3)

with *R* the particle radius and *a* the contact radius particle/substrate. Because the contact radius *a* is very small compared with the particle radius, a/1.4R will be much smaller than κ , which is normally close to unit. Hence, particles are much easier to roll off a substrate than to slide them by the removal forces and sliding is actually not likely to happen during scrubbing. As the brush/wafer pressure increases, owing to large contact area brush/particle because of the brush deformation, the adhesion force brush/particle can be very big compared to the adhesion force particle/wafer. In such a case, particles can be lifted off directly. As a result, rolling and lifting can be dominant particle removal mechanisms during brush scrubber cleaning.

In this paper we further elucidate the mechanisms of particle removal during brush scrubber cleaning for nano-sized slurry particles by investigating the particle radial surface concentration as a function of cleaning time. In the theoretical part, we first establish some models based on only lifting, only rolling and lifting + rolling mechanisms. Afterwards, the uniformity of the particle radial surface concentration of a wafer and the processing time effect on the particle removal is investigated. The models are used to predict the experimental results. By doing so, the removal mechanisms of scrubbing under varied scrubbing conditions are determined. Finally, some experimental evidences on the particle removal mechanisms are shown.

EXPERIMENTAL

Controlled contamination of wafers was done using an immersion based contamination procedure, followed by an over-flow rinse and a Marangoni dry. The particle was 34 ± 6 nm SiO₂ Clariant slurry particle and the substrate was silicon nitride.

Electrochemical Society Proceedings Volume 2003-26

Before use, the wafers were cleaned using an O₃-last IMEC-clean [8] in a STEAG automated wet-bench. After contamination, the particle surface concentration is $1.6 \times 10^{10} \text{ #/cm}^2$, which equals a 16% surface area coverage by particles.

The average added haze of the wafer after pre-clean, after controlled contamination and after brush scrubber clean are determined by light scattering measurements using a KLA Tencor SP1^{DLS} apparatus with dark field, wide collection angle and oblique incident beam. The particle surface concentration was investigated by measuring the haze of a wafer based on the proportionality between the particle surface concentration and the added haze of a wafer [9,10,11]. The final particle removal efficiency (PRE) is calculated by using the following formula.

$$PRE = \left(1 - \frac{Haze_BrushClean - Haze_CC}{Haze_CC - Haze_PreClean}\right) \times 100$$
(Equ. 4)

with Haze_PreClean, the initial average haze before the controlled contamination Haze CC, the average haze after the controlled contamination

and Haze BrushClean, the average haze after the brush scrubber clean

Before scrubbing, all the contaminated wafers were aged for 24hours in a 0% relative humidity. During the tests, two scrubber systems with double-sided brushes were used: Ontrak Scrubber from Ontrak Systems and Damasclean from Mattson.

THEORETICAL

Time effect on particle removal across the wafer during brush scrubber cleaning

During the brush scrubbing, the wafer rotates at an angle velocity of ω (see Figure 2). As a result, the linear velocity v_{linear} of wafer at particle radial position *x* can be described as:

$$v_{linear} = \omega \cdot x$$
 (Equ. 5)

According to Figure 2, the contact area between the brush and the wafer is the same for all *x*. During one cleaning rotational cycle, the actual cleaning time $\tau(x)$ is:

$$\tau(x) = \frac{2L_{ab}}{v_{bnear}} = \frac{2L_{ab}}{\omega \cdot x} \Longrightarrow \tau(x) \propto \frac{1}{x}$$
 (Equ. 6)



where L_{ab} is the width of the contact area between the brush and the wafer.

Taking into account that lifting and rolling as the principal mechanisms of particle removal during scrubber clean, the particle removal efficiency can be predicted as a function of cleaning time and radial distance.

Lifting model: Assuming lifting is the only particle removal mechanism during brush scrubbing, particle removal on the full wafer surface should only vary with the brush/wafer actual contact time. Therefore, the particle surface concentration as a function of scrubbing time and the wafer radial distance after a brush scrubber clean, based only on lifting model, can be formulated as:

$$\frac{\partial c(x)}{\partial t} = -\frac{A}{x} \cdot c(x) \tag{Equ. 7}$$

where A is a fit parameter, which should be influenced only by the brush/wafer pressure.

<u>Rolling model</u>: Assuming rolling is the dominant particle removal mechanism from substrate during brush scrubbing, particles should have a trend to move from the centre of a wafer to the edge of it. As the brush rotates like shown in Figure 2, the particle, deposited on the wafer and contacting the brush, should be able to move in the cross direction of the brush-alignment. In other words, a particle at a radial distance x in Figure 3 contacting the brush should be able to have a moving distance of D after a cycle of brush scrubbing. As a result, after the cycle of scrubbing the particle has moved a distance of d_x towards the wafer edge, a centrifugal distance, which can be described by the following formula:

$$d_x = \sqrt{x^2 + D^2} - x \qquad (Equ. 8)$$

After a second brush scrubbing cycle, the particle undergoes a similar process, which results a particle moving distance D_1 and a centrifugal distance d_{xl} as shown in Figure 3. Obviously, particles deposited on the wafer surface follow a spiral road towards the wafer edge and get removed after a certain number of brush scrubber cycles if the rolling plays as the dominant removal mechanism. If we assume the particle moving distance D during a brush scrubbing cycle is



Figure 3: Schematic cross-view of particle's moving towards the wafer edge during brush scrubber cleaning.

only proportional to the actual cleaning time $\tau(x)$, then the above equation can be rewritten as:

$$d_x = \sqrt{x^2 + \frac{B^2}{x^2} - x}$$
 (Equ. 9)

where *B* is a fit parameter. If we define an average centrifugal velocity v(x) during a brush scrubbing cycle, then it can be described as

$$v(x) = \frac{d_x}{1/\omega} = \omega \cdot \left(\sqrt{x^2 + \frac{B^2}{x^2}} - x\right)$$
(Equ. 10)

If the particle mass balance in the circle region between the wafer radial distance of x and x+dx in Figure 3 during scrubbing time dt is considered, the surface concentration on the wafer surface as a function of the scrubbing time t and the radial distance x can be formulated as:

$$\frac{\partial c(x)}{\partial t} = -\frac{c(x) \cdot v(x)}{x} - c(x) \cdot \frac{\partial v(x)}{\partial x} - v(x) \cdot \frac{\partial c(x)}{\partial x}$$
(Equ. 11)

<u>Rolling + lifting model:</u> If we assume that both lifting and rolling occur in a scrubber clean the change in particle surface concentration as a function of cleaning time equals:

$$\frac{\partial c(x)}{\partial t} = -\frac{A}{x} \cdot c(x) - \frac{c(x) \cdot v(x)}{x} - c(x) \cdot \frac{\partial v(x)}{\partial x} - v(x) \cdot \frac{\partial c(x)}{\partial x}$$
(Equ. 12)

Basically, it is the mergence of Equ.7 and Equ. 11 with the fit parameters A and B.

140

After contamination, a nitride wafer receives a brush scrubber clean and the haze

map of the wafer is shown in Figure 4b: a cleaned circle is achieved in the region close to the wafer centre while the particle surface concentration in the region close to the edge remains the same as the before one scrubbing. Further tests are done by varying the scrubbing time while keeping other conditions all the same. From Figure 4, we can easily conclude that the brush scrubber clean is a heterogeneous process: a cleaned area is first achieved in the wafer centre and extends to the



d)55s, avg.PRE 86%, e)175s, avg.PRE 99.8%, f)600s, avg.PRE 100% 75-98 50-75 25-50 0-25 PRE (%) 98-100 Figure 4: removal efficiency versus scrubbing time and radial distance of a wafer; brush wafer distance -2.0mm (high pressure), chemical pH10 ammonia.

wafer edge as the scrubbing time increases.

Lifting model is first used to explain the results. When A is determined by fitting the experimental scrubbing data in Figure 4b considering the radial distance of the

cleaned area, the particle surface concentration after scrubbing can be predicted by Lifting model (see Figure 5). Obviously, the lifting mechanism is not able to explain all the results in Figure 4: the particle surface concentration in the region close to the wafer edge remains the initial value after contamination even after a relatively long scrubbing time experimentally while it drops too fast according to the lifting model prediction.

Rolling model comes to predict the results. Since there is no analytical solution to Equ. 11, a numerical way is used to solve it



5: Figure particle radial surface concentration after scrubbing versus cleaning time predicted by Lifting model.

with some approximations. When *B* is determined by fitting the experimental scrubbing data in Figure 4b in the same way as determining Α. the particle surface concentration after scrubbing should be able to be described by Rolling model (Figure 6). Although Rolling model is able to predict the particle surface concentration after a relatively short scrubbing time and good to predict the sharp difference between the cleaned and noncleaned, it cannot explain all the results in Figure 4: it takes a much longer time to roll all the particles completely out of the wafer according to the above equation than the experimental result.

Lifting + Rolling model is used to interpret the results, a numerical approach being applied to approximate Equ.12 owing to no analytical solution to it. The particle surface concentration after scrubbing is then calculated by this model using the determined values of Aand B from Lifting model and Rolling model (see Figure 7). Clearly, the particle surface concentration after scrubbing determined by Rolling + Lifting model agrees much better with

By scrubbing a delta-contaminated chemical, we clearly find that particles can be processing clean nitride wafers with contaminated brushes, we find that there is no re-deposition of particles from the brushes to the wafer if dilute ammonia is used (Figure 9). As a result, the particle redistribution in Figure 8 can only be caused by rolling. However, based on the prediction of Rolling model, the rolling mechanism cannot explain the particle removal close to the wafer edge in a reasonable cleaning time such as 3min. Therefore, we can conclude that both lifting and rolling happen during a scrubber clean.







Figure 7: particle radial surface concentration versus cleaning time predicted by Rolling & lifting model.

Rolling + Lifting model agrees much better with the experimental results shown in Figure 4 than the one determined either by Lifting model or Rolling model.

By scrubbing a delta-contaminated wafer using dilute ammonia as the in-situ chemical, we clearly find that particles can be displaced on the same wafer (Figure 8). By



Figure 8: distribution of particle surface concentration after contamination (left) and after brushing (right); brush/wafer distance – 0.6mm (low pressure), pH10 NH₄OH, 120s.

Further tests with a relatively low brush/wafer pressure and short cleaning time such as 5s or 10s shows that there always exists a sharp difference between the cleaned region and the non-cleaned one (Figure 10). As already discussed in this paper, these sharp difference phenomena are mainly the result of the rolling mechanism. Compared with a high brush/wafer pressure in Figure 4, especially Figure 4b and c, the difference between the cleaned and non-cleaned is much more sharper after scrubbed with a low brush/wafer pressure shown in Figure 10. As mentioned in the

introduction, a higher brush/wafer pressure results in a bigger brush/particle adhesion, which makes the lifting criterion in Equ.1 more likely to satisfy. On the other hand, according to Rolling model, rolling is basically a mechanism more associated with the region close to the wafer centre for a short cleaning time. As far as the region close to the wafer edge is concerned, the lifting becomes more dominant since it would take ages to roll particles completely out of the wafer if only by the rolling mechanism. Required a still



Figure 9: particle surface concentration versus the number of wafers processed after running the clean wafers with contaminated brushes.



Figure 10: removal efficiency versus radial distance of a wafer; cleaning time 10s, brush/wafer distance -0.6mm (low pressure), pH10 ammonia.

143

relatively long cleaning time, the particle removal by lifting on the wafer edge is regarded as a long process. In a word, rolling is more responsible for the particle removal in the region close to the wafer centre for a short cleaning time or with a low brush/wafer pressure while lifting is more responsible for that in the region close to the wafer edge for a long cleaning time or with a high brush/wafer pressure.

CONCLUSIONS

Scrubbing is a heterogeneous process: a cleaned area is first achieved in the wafer centre and extends to the wafer edge as the processing time increases.

The particle removal mechanisms are studied by investigating the surface radial concentration of particles after scrubbing. Based on rolling and lifting removal mechanisms, three models (Rolling model, Lifting model, Lifting + rolling model) are used to predict the particle radial surface concentration as a function of the scrubbing time. Rolling + lifting model is found to be the best to describe the particle removal behaviour of scrubbing.

Both rolling and lifting are believed to be the particle removal mechanisms during a brush scrubber clean. Rolling is more responsible for the particle removal in the region close to the wafer centre, for a short cleaning time and with a low brush/wafer pressure while lifting is more responsible for that in the region close to the wafer edge, for a long cleaning time and with a high brush/wafer pressure.

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EVALUATION OF MEGASONIC CLEANING SYSTEMS FOR PARTICLE REMOVAL EFFICIENCY AND DAMAGING

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In future semiconductor technology generations cleaning processes will face the challenge of removing nano-particles with no damage to fragile structures and virtually no etching of the substrate. In this study we have evaluated the capabilities of a representative set of present megasonic cleaning tools to meet this challenge in process conditions where the etching of thermal silicon dioxide was lower than 0.5 Å. The tests vehicles for particle removal and damaging consisted in 34 nm SiO₂ particles on hydrophilic Si wafers and in poly-on-gate lines of line-width ranging from 150 to 70 nm, respectively. No tool reached the target of high particle removal efficiency (PRE) and low damage to the 70 nm lines in the present series of tests. Lower damage could only be obtained at the cost of lower PRE, by decreasing the megasonic power. Wafer maps for PRE and damage showed patterns that were tool-specific. Only two systems out of five seemed to show a simple direct correlation between PRE and damage at wafer level, indicating that more fundamental research is needed to understand the cleaning and damaging mechanisms in megasonic systems.

INTRODUCTION

In semiconductor manufacturing, as features sizes are scaling down below 100 nm, particles with a diameter of a few tens of nanometers need to be considered as killer defects. For example with the 90nm technology node particles of a size larger than 45nm are believed to be potential killer defects for devices in chips.¹ For several reasons related to substrate consumption budget, cost, and environmental impact, present cleans make use of diluted chemistries with low etching capability and need additional physical mechanisms, such as megasonic agitation, to remove contaminant particles.² As particle size decreases, the ratio of adhesion force over cleaning force increases, thereby potentially compromising the particle removal efficiency (PRE).³ On the other hand, wafer surfaces may present fine structures with fairly high aspect ratios, such as gate electrodes or low k isolation patterns, which become vulnerable to sideward impact by physical forces.^{4,5} The combination of all these trends results in a collapse of the process window to the extent that cleaning of nano-particles is becoming a major challenge in production and the future use of traditional cleaning methods is questioned.

Previous studies have demonstrated that, even though cleaning of nano-particles is becoming increasingly more difficult as particle size decreases, it is actually possible to

Electrochemical Society Proceedings Volume 2003-26

remove particles with a diameter as small as about 30 nm by megasonic cleaning.^{6,7} PRE was shown to depend strongly on the presence of dissolved gas in the cleaning solution, indicating that cavitation was playing an important role in the cleaning mechanism.^{8,9} The decrease in PRE at smaller particle size was associated with a decrease in cleaning uniformity.

In this work various megasonic cleaning systems were evaluated for removal efficiency of nano-particles, cleaning uniformity, and damaging of fragile structures, providing a snapshot of the capabilities of present tools to respond to the new challenges. Additionally comparison of wafer maps for PRE and damaging was used to better characterize the relationships between PRE and damaging.

MATERIALS AND METHODS

The cleaning tests were performed in various systems (A, C to F) differing by their configuration (batch or single-wafer, position of transducers, carrier), solution flow (recirculation or single-pass), transducer operation (continuous or multiplexed), and wafer size (200 or 300 mm) (Table 1). Transducer frequencies ranged from 0.7 to 1 MHz. The effect of dissolved gases was studied by comparing results obtained with degassed and aerated DIW. PRE was determined with hydrophilic 200 or 300 mm Si wafers contaminated with SiO₂ particles of 34nm diameter purchased as slurry (Clariant Elexsol). Wafers were contaminated using an immersion based controlled contamination (CC) procedure and used within a few hours after preparation.¹⁰ Particles numbers were determined using light scattering on a KLA Tencor SP1^{TBI} using the haze channel.^{10,11} Particle removal efficiencies (PRE) were calculated from measured particle counts after CC and after clean, taking the initial count pre-CC into account.

Tool	Version	Туре	Flow	Transducer operation	Wafer size (mm)	Carrier
А	α-design	Batch	Single-pass	Continuous	300	No
С	Demo	Batch	Recirc.	Multiplexed	200	Low-mass
D	Commercial	Batch	Recirc.	Multiplexed	200	No ¹
Е	Commercial	Batch	Recirc.	Continuous	200	Low-mass
F	α-tool	SW ²	Single-pass	Continuous	200	Edge grip

Table 1. Overview of tested megasonic cleaning tools.

Wafer moved up and down during process ² single wafer

The test vehicle for damaging consisted in 200 mm wafers with poly-on-gate lines that were inspected by laser-light scattering (KLA-Tencor AIT) and SEM (Philips XL810). The lines were 8 mm long and about 170 nm tall, with widths and aspect ratio

Electrochemical Society Proceedings Volume 2003-26

ranging from about 150 to 70 nm and about 1.1 to 2.5, respectively (Fig. 1). The lines were printed in groups of nine, differing by line-width and spacing. External lines in groups of narrow spacing were printing thinner as a result of so-called proximity effects during photolithographic exposure (see Fig. 1, left). Finally the pressure distribution at the surface of wafers during cleaning was determined with wafers covered with a pressure indicative sensor film (Pressurex Micro, from Sensor Products Inc.).¹²



Fig. 1. SEM view of poly-gate lines with line-width of about 140 nm (left) and 70 nm (right), respectively.

RESULTS AND DISCUSSION

With all megasonic-cleaning tools damaging of poly lines showed up in SEM inspection as the removal or bending of small pieces of line with a length of about 1 to 2 μ m (Fig. 2). The localized character of damage suggests that cavitation was probably the cause. Full wafer inspection with a KLA-Tencor AIT could only detect the removed pieces of line but allowed to determine defects statistics and the spatial distribution of defects on wafers.



Fig. 2. Representative SEM views of 70 nm poly-gate lines damaged by megasonic cleaning, showing removed (left) and bended (right) pieces of line.



<u>Fig. 3.</u> Poly-gate lines damage frequency distribution as a function of line-width and aspect ratio (tool E, APM 1:1:80 at 30°C, 5 min, 100 % power).

Figure 3 shows a typical frequency distribution for damage of these poly lines as a function of line-width and aspect ratio. Calculations took into account the area covered by groups of lines and the thinning of external lines with narrow spacing. Line-width bins were defined with a range of about ±5 nm from 70 to 110 nm and a range of about ± 10 nm from 120 to 150 nm. Comparable results were obtained when taking the length of lines into account

instead of the area. The distribution is characterized by a strong increase in damage frequency for line-widths below 100 nm. This observation is valid for all tools and process conditions tested in this study. It indicates that present megasonic cleaning tools will suffer a dramatic reduction in process window with new technology generations.

In future generations the process window will be defined by the achievement of high removal efficiency for nano-particles with no damage to fragile structures and virtually no etching of the substrate. In Fig. 4 the density of megasonic defects per wafer for 70 nm poly lines is compared to the PRE for 34 nm SiO₂ particles under process conditions where etching of thermal oxide was less than 0.5Å in most cases. In most conditions only one poly-gate line wafer was used per test. Reproducibility was checked by performing a few tests with two wafers, giving a range of variation typically of about 10 % for the total number of defects per wafer. Figure 4 shows three groups of data points, labeled I to III. Group I corresponds to cleans performed at high power in degassed solutions (< 0.3 ppm O₂, single-pass). PRE was close to zero while damage was relatively high. Group II corresponds to cleans performed at high power in aerated solutions under different process conditions (chemistry, concentration, temperature). Gas dissolution resulted in significantly higher PRE but damage levels remained relatively high, increasing even in case of tool F. Finally group III gives results from tools A, C, and F where megasonic power was decreased for a given set of process parameters with aerated solution. The presence of dissolved gas in the cleaning solution as a necessary condition to remove nano-particles indicates that the cleaning mechanism was not due to acoustic streaming (Eckart and Schlichting streaming) or vapor cavitation, but rather to gas cavitation phenomena (micro-streaming, bubble implosion).^{8,13,14} Damaging with degassed solutions probably indicates that vapor cavitation occurred under these conditions. Only decreasing the power proved to be efficient in decreasing the number of megasonic defects, albeit at the cost of a lower PRE (group III). Apparently, from this series of tests, no tool was able to reach the target of high PRE with no damage.

Electrochemical Society Proceedings Volume 2003-26



<u>Fig. 4.</u> Damage to 70 nm poly-gate lines as a function of PRE for 34 nm SiO₂ particles for tools A to F under various process conditions (see text). The asterisk (*) points to data points where etching of thermal oxide was higher than 0.5Å.

Figure 4 shows that PRE and damaging are directly correlated to megasonic power. In this line it is generally believed that PRE non-uniformity at wafer level is caused by a non-uniform acoustic pressure distribution, with lower PRE areas corresponding to lower pressures. However a close look at wafer maps obtained in this study for PRE and damaging showed that there was usually no simple correlation between PRE, damaging, and power at wafer level. This will be illustrated in the case of tools C, E, and F.

Wafer maps for PRE and damaging for tools C, E, and F are given in Fig. 5. In tool C and E the array of transducers was firing the wafers from bottom up. Patterns obtained in different process conditions were similar, differing mainly by the level of PRE or damage. Both types of maps show patterns that were tool-specific. The patterns for tool C were characterized by vertical stripes, those of tool E by higher PRE and damage along the vertical diameter, while tool F presented circular patterns corresponding to the spinning motion of the wafer during cleaning.

Although wafer maps for PRE and damaging showed striking similarities, there seemed to be a direct correlation between PRE and damaging at wafer level only in the case of tools A and E. Higher damage was observed in areas of higher PRE, as shown for tool E in Fig. 5. With tool C, the opposite was observed: stripes with higher PRE presented a lower damage and vice versa. The pressure distribution across the wafer surface was determined with pressure sensitive films, revealing stripes of higher pressure above the center of the elements of the transducer array (Fig. 6). Thus higher pressure corresponded to higher damage but lower PRE. Tool D also had multiplexed transducers, but mounted in arrays in the sidewalls of the megasonic tank, while the wafer was moved

up and down during cleaning. In this case no stripe pattern was observed on the wafer maps that presented no clear correlation between PRE and damaging. Finally with tool F the highest damage was observed in an outer ring of intermediate PRE (85-95 %), while other rings of higher (95-100 %) or lower (50-85 %) PRE presented a lower damage.



<u>Fig. 5.</u> Wafer maps for PRE (top, 34 nm SiO₂ particles) and megasonic damage (bottom, 70 nm poly-on-gate lines, NI = not inspected) for tools C, E, and F. Cleaning conditions: aerated diluted APM solutions at 20-30 °C, with an average PRE in the range of 70-90 %.





CONCLUSIONS

We have evaluated the capabilities of a representative set of present megasonic cleaning tools to remove nano-particles with low damage in process conditions where the etching of thermal silicon dioxide satisfied specifications for the 70 nm technology node. The tests vehicles for particle removal and damaging consisted in 34 nm SiO₂ particles on hydrophilic Si wafers and in poly-on-gate lines of line-width ranging from 150 to 70 nm (aspect ratio 1.1 to 2.5), respectively.

All tools were capable of achieving high particle removal efficiencies (PRE) of about 80 % or higher for the nano-particle challenge. Damaging by megasonic was low for lines wider than 100 nm but started to increase dramatically for smaller line-widths. Among the parameters tested megasonic power had the most significant influence on damage. Decreasing megasonic power allowed to decrease megasonic damage to 70 nm lines, albeit at the cost of a lower PRE. As a consequence no tool reached the target of high PRE and low damage in the present series of tests.

PRE was limited by cleaning non-uniformity at wafer level, which showed toolspecific patterns. Wafer maps for damaging also showed tool-specific patterns. However in three systems out of five there was no simple direct correlation between PRE and damage at wafer level, indicating that more fundamental research is needed to understand the cleaning and damaging mechanisms in megasonic systems.

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Electrochemical Society Proceedings Volume 2003-26

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MECHANICAL RESISTANCE OF FINE MICROSTRUCTURES RELATED TO PARTICLE CLEANING MECHANISMS

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The effect of wet cleaning processes to remove deposited particles was investigated in terms of potential damage occurring on simplified IC microstructures. It was first concluded that wet processes are compatible with technology lower than 0.05 μ m except for structures presenting only van der Waals interactions with the substrate, because of detrimental induced capillary forces. The drag forces able to remove the particles are not dangerous for microstructures. However, the shock waves enabling critical particles to be removed can greatly affect structures even presenting a modest aspect ratio of two.

INTRODUCTION

According to the International Technology Roadmap for Semiconductors (1), smaller and smaller particle sizes will have to be eliminated as the device dimensions shrink. In the near future, particles would probably be the most challenging type of contamination as the conventional SC1 (2) removal mechanism, based on controlled consumption of the layer under the particle, would be rapidly prohibited. Indeed, the active layer dimensions (implanted layers, silicon on insulator, etc.) are now approaching the thicknesses required for particle removal by under-etching. This work follows a first contribution (3) where theoretical capabilities and limitations of wet and alternative cleaning processes adapted to fine particle removal were discussed. In this paper, the effects of capillary forces, drag forces and choc waves necessary to remove particles were investigated in terms of mechanical damages on device microstructures. These effects have to overcome van der Waals attractive forces exerting on particles without breaking the fragile patterns. Fundamental interactions taking place during cleaning processes were considered independently whatever the technological way chosen to produce them, such as steam laser cleaning, fast evaporation, high velocity sprays, droplet jet and megasonic bath and spray. Repulsive electrostatic forces that are generally negligible compared to van der Waals forces -acting at contact but very useful to prevent from re-adhesion- have not been considered in this paper for simplification purpose.

MECHANICAL RESISTANCE OF MICROSTRUCTURE

In a first intent, two simplified structures (infinite patterned line presenting different aspect ratios) were studied for two extreme cases. The first type of structure is referenced to "Posed" structure, the line was simply deposited on the substrate (see figure 1). In the second one, called "Bulk" structure, the line was patterned in the same material as the substrate without any interface (see figure 3). The strength of actual structures is supposed to lie within these 2 extreme cases.

Posed structure

In this case, only weak interactions originated from van der Waals (vdW) forces coexist between the patterned line and the substrate. Typical examples are: lines of

153

photoresist, noble metals deposited by CVD on SiO₂ and also layers presenting a great affinity with the substrate but affected by an organic contamination layer. As presented in figure 1, the line may be rocked down by a couple produced by the effects of the different cleaning processes. This couple is considered to originate from a constraint parallel to the substrate uniformly distributed throughout the entire line surface. In this particular case, the same couple number is produced by the total external force applied at mid height: h/2 of the structure. As indicated by equation [1], the break down condition is reached when the couple generated by the external force *F* overcomes the return couple due to the vdW forces F_{vdw} between line and substrate (note that all these forces are expressed by unit of line length). Using the derivative form of equation [4] for the expression of the vdW force per unit area of contact: dF_{VdW} , the breakdown conditions are linearly dependent to the line thickness: e -which corresponds also to the technology node- when written as a function of the aspect ratio a = h/e (equation [2]).



$$F\frac{h}{2} \ge \int_{0}^{e} x \ dF_{vdw} = \int_{0}^{e} x \ \frac{A}{6\pi \ h_{0}^{3}} \ dx \qquad [1]$$

$$F \ge \frac{A}{6\pi \ a \ h_0^3} e$$
 [2]

With: *A*: Hamaker constant *h*₀: Lennard-Jones distance

Figure 1: Schematic of the "Posed" structure.

Results shown in figure 2 were calculated using a Hamaker constant corresponding to polystyrene -as an organic- on silicon oxide in water, given in Table 1 (PSL/SiO₂).



Figure 2: Force by unit of line length necessary to break a Posed structure (A = $1.0 \ 10^{-20}$ J).

Bulk structure

The bulk structure corresponds to the most favorable case where a line was made of the same material than the substrate with no physical interface in-between. Calculation of the breakdown force has been performed by finite element using a home-made thermomechanical software: CASTEM (4). The breakdown criteria has been chosen when the maximum principal stress component, at the basis of the line, exceeds 1 Gpa. Figure 4 presents an example of the distribution of the maximum principal stress component at the bottom of the line: the maximum principal stress component corresponds to the orthoradial component of the stress tensor taken from the center of curvature at the bottom of the line as represented in the insert of figure 4. This component is positive while the bottom corner of the line is in tension. At the very moment, this component

exceeds our criterion, a crack will propagate in silicon. The strength of a bulk line is related in a large extend to the radius of curvature present at the bottom of the line.



Figure 4: Distribution of the orthoradial component of the stress tensor (cracks are supposed to propagate in mode I) for a bulk line submitted to an external force (10 μ N/ μ m) uniformly distributed at one side of the line (or concentrated at h/2). Insert: definition of the radial and orthoradial components of the stress tensor.

In figure 5, calculations have been performed for bottom radius of 1 and 2.5 nm. Again, the breakdown forces are quasi linear with the line thickness for a given aspect ratio. Bulk structures with a small bottom radius of 1 nm present a strength 20 times higher than a Posed structure linked to the substrate by simple vdW interactions.



Figure 5: Force by unit of line length necessary to break Bulk lines. Bottom radius are set to 1 and 2.5 nm on left and right figures respectively.

INTERACTIONS ON PARTICLES AND MICROSTRUCTURES

Interactions liable to act on both particles and microstructures during cleaning processes were estimated to compare structure breakdown and particle removal thresholds.

155

Van der Waals forces

The vdW forces of a spherical particle or an infinite flat particle both on a perfectly flat substrate are given by equations [3] and [4] respectively.

$$F_{vdW} = \frac{AR}{6h_0^2} \quad [3] \qquad \qquad F_{vdW} = \frac{AS}{6\pi h_0^3} \quad [4]$$

Where R represents the particle radius, h_0 the particle-substrate distance with a minimum equal to the Lennard-Jones distance: 0.4 nm, *A* the Hamaker constant and *S* the facing particle and substrate surface. From data and formula given by Israelachvili (5), the Hamaker constants for different particle/substrate materials can be calculated. Results reported in Table I show that on SiO₂ substrates, vdW forces for usual particle materials can vary by one order of magnitude according to the media.

Media	Al ₂ O ₃ /SiO ₂	SiO_2/SiO_2	PSL / SiO ₂
Water	1.6 10 ⁻²⁰ J	6.5 10 ⁻²¹ J	1.0 10 ⁻²⁰ J
Air	9.6 10 ⁻²⁰ J	6.3 10 ⁻²⁰ J	7.5 10 ⁻²⁰ J

Table I: Hamaker constants in water and in air calculated from reference (5).

The difference of vdW attractions between a reference rigid and spherical particle and actual particles is investigated here. The consequence of the non ideality of the actual particles: flattening, non specific shape, roughness, partially embedded, etc. can finally be considered as an additional flat surface in contact with the substrate. In this work, the shift to ideal spherical and rigid spheres (of radius R) was arbitrarily expressed by the fraction f equal to the surface of the particle in contact with the substrate divided by πR^2 (equation [5]). f is null for an ideal spherical particle and reaches 1 for a particle presenting the maximum surface in contact, i.e. a semi-sphere (see figure 5). For a quasi-spherical particle presenting a small flat contact area, the total vdW forces can be considered as the sum of the contributions from the non deformed particle and the contact rapidly dominate the spherical particle contribution. The ratio \Re between the vdW attraction of actual and ideal -rigid and spherical-particles can be approached by the equation [6].

$$f = \frac{S}{\pi R^2} \qquad [5] \qquad \qquad \Re = \left(\frac{AR}{6h^2} + \frac{AS}{6\pi h^3}\right) / \left(\frac{AR}{6h^2}\right) = 1 + f \frac{R}{h} \qquad [6]$$

Results have been plotted in figure 5 for particle sizing from 10 to 150 nm. It can be seen that the vdW forces increase rapidly with the non ideality of the particles and can reach more than 2 orders of magnitude greater than the ideal particle. This effect decreases with the particle size. Finally, due to the large range of variation of the Hamaker constant and the important impact of the real shape of the particles, vdW interactions can vary to a very large extent for the different existing particle types. As the most adhering particles have even to be removed, we have arbitrarily considered that vdW forces are 2 orders of magnitude above the system: rigid sphere of Al₂O₃ on SiO₂ substrate -presenting the highest Hamaker constant (Table I). Based on this concept, the equation [3] can still be used for particles with the pseudo Hamaker constant A' = 100 x $1.6 \ 10^{-20}$. This approach enables a very wide majority of actually observed particles to be covered but clearly does not take into account the extreme cases of flat shape particles made of materials leading to very high Hamaker constants. The substrate roughness was not considered as it generally decreases the contact areas leading to lower vdW forces.



Figure 5: Ratio \Re between van der Waals forces calculated for the reference rigid sphere and actual particles presenting a flat surface in contact. This surface is given as a fraction of the area of the sphere cross section which represents the maximum contact surface for a given particle size.

157

Capillary forces

In the case of a spherical particle, the maximum capillary force is obtained when the liquid wets the particle material perfectly (contact angle $\theta = 0$) and the gas/liquid interface is acting on the whole particle perimeter:



Figure 6: Schematic of the maximum capillary force acting on a particle.

If as represented in figure 7, the liquid wets the material of the lines, Laplace law shows that the pressure is lower in the liquid. If no liquid is present in the adjacent interval, the de-pressure tends to break the lines. The capillary force acting on a line can be approximated by equation [8], where L is a unit of line length (the perimeter surface tension effect is here neglected). At fixed aspect ratio, this force is independent of the technology node.

No liquid
$$F_{\gamma} = \frac{2 \gamma_{\rm lg} \cos(\theta) h}{e} = 2 \gamma_{\rm lg} \cos(\theta) a$$
 [8]

Figure 7: Capillary forces acting on lines when the material is wetted by the liquid.

Drag forces

In the case of a spherical particle placed in a flow of velocity V, the drag force is given with a good approximation (7) by the Stokes law up to a Reynolds number of ten. For the very small particles considered in this study, the Reynolds number stays under this value even for high liquid velocities (e.g. for a 100 nm particle, a Reynolds number Re = 10 corresponds to a water flow velocity of 100 m/s !). In the case of a particle deposited on a surface, an additional constant of 1.7 accounting for the effect of the surface must be

added (8): $F_{D_{rag}} = 1.7 \ 3\pi \ \mu \ R \ V$ [9] Where μ represents the fluid viscosity: $10^{-3} \ kg/m.s$ for water at 20°C. This force is theoretically only able to roll the particle on the surface. It can be expected that an asperity on the particle or on the substrate will transform this tangential force to a lift-off momentum (9, 10). The drag forces are generally higher for case non spherical particles. The drag force applying on an

isolated patterned line can be approached by the case of an infinite plate, treated in (7) for Re < 10:

$$\frac{F_{Drag}}{L} = \frac{1}{2} C_x \rho V^2 \qquad [10] \qquad \text{With}: C_x = \frac{8\pi}{\text{Re}} \frac{1}{(2.2 - Log \,\text{Re})} \qquad [11]$$

$$Re = \frac{\rho V h}{r} = \frac{\rho V a}{r} e \qquad [12]$$

Forces generated by shock waves

The instantaneous overpressure induced by a shock wave -so called "water hammer" on a surface S is given by equation [13]. $F_{shock} = S \rho c V$ [13]

μ

μ

Where ρ represents the mass density of the media, V the media velocity and c the wave propagation in the media (c = 1500 m/s in water). In case of a spherical particle, S is assimilated to the cross section area πR^2 : see equation [14]. For a line, the surface is equal to Lxh and leads to equation [15].

$$F_{shock} = \pi \ R^2 \rho \ c \ V \quad [14] \qquad \qquad \frac{F_{shock}}{L} = h \ \rho \ c \ V = \rho \ c \ V \ a \ e \quad [15]$$

RESISTANCE OF LINES DURING PARTICLE REMOVAL

Capillary forces

To remove particles, capillary forces have to overcome vdW interaction. Using equation [3] and [7] leads to the condition: $2\pi \gamma_{lg} \ge A'/6h_0^2$ [16] which is not satisfied when using our A' proposed value. Particle removal efficiency does not depend on particle dimensions but even for perfectly wetted materials, capillary forces are not able to overcome vdW interactions for all particle types. So, it is difficult to envisage a cleaning process based on capillary forces only. Anyway, the use of wet chemistries induces capillary forces on the microstructures. Calculations presented in Figure 8 show the ratio between capillary and breakdown forces from equations [8] and [2] respectively, for the worse case: Posed structure and when materials are perfectly wetted ($\theta = 0$).



A for Posed structure: 1.10^{-20} J Water: 0.072 N/m Material: SiO₂ ($\theta = 0$)

Figure 8: Breakdown thresholds for Posed structures in water. The dashed line is relative to a bulk structure with an aspect ration of 5 and a bottom radius of 1 nm, given for comparison.

Structures presenting an aspect ratio lower than 2 resist quite well to surface tension even in the worse case. As shown by the dashed lines, for real Bulk structures the effect of surface tension under wet processes is not an issue until an aspect ratio of 5. Nevertheless, we have to be vigilant for fragile structures (e.g. Posed structures) presenting aspect ratios above 2, especially in the particular case of photo resist development process.

Drag forces

Equalizing vdW and drag forces from equations [3] and [9] enables to calculate the flow velocity necessary to remove the particles: $V = A'/(30.6 h_0^2 \pi \mu)$ [17]. This velocity does not depend on particle dimension and equal 52 m/s in the considered conditions. Injecting this number in equation [10] gives the forces acting on the lines for fixed aspect ratios. Figure 9 shows that drag forces necessary to remove particles can affect the more fragile lines down 0.16 μ m only but are not really dangerous for most of the structures.



Figure 9: Comparison between the drag forces exerted on lines necessary to remove all the particles and structure strength range (aspect ratio: 2).

Shock waves

The speed of the media necessary to remove particles is obtained by equalizing vdW expression [3] and the shock wave force acting on a particle [14]: $V = A'/(6 \pi h_0^2 R \rho c)$ [18]. This velocity has to be increased to remove smaller particles. V is then replaced in equation [15]. If we consider that the particle to be removed are 50% larger than the technology node (ITRS), it is possible to replace R by e/4. Then the force acting on the lines does not depend on the technology node anymore: $F_{shock} / L = 2aA'/(3h_0^2 \pi)$ [19].



Figure 10: Comparison between shock waves originated forces exerted on the lines to remove critical particles and structure strength range (aspect ratio: 2).

As seen in figure 10, for an aspect ratio of 2, the effects of the shock waves necessary to remove the critical particles can break patterned lines. The technology threshold strongly depends on the actual cohesion between patterned structures and substrate. Even the more

Electrochemical Society Proceedings Volume 2003-26

robust line are destroyed for technology down 0.05 μ m. In this case a slight underetching of 0.2 nm (1 monolayer) can greatly improve this threshold.

CONCLUSION

The force of adhesion of a patterned microstucture on a substrate can vary by a factor of 20 according to the type of bondings, from simple van der Waals interactions to covalent bounds between same materials without any interface. In the case of a Bulk structure presenting strong interactions with the substrate, the bottom radius is a key parameter for mechanical resistance. In order to take into account most of the particle adhesion forces for the different actual types of particle shapes and materials, a pseudo Hamaker constant A', two orders of magnitude higher than the one calculated for conventional particle and substrate materials, was used in the model of the rigid sphere. The capillary forces acting on the microstructures during liquid processes are not an issue for usual cases up to aspect ratio of 5. Therefore, wet processes could be still effective technology for 65 nm node and beyond. On the other hand, great attention has to be paid for weakly bounded structures presenting aspect ratios above 2, e.g. photo resist. Unfortunately, capillary forces cannot remove highly adhered particles from the substrate even so, they could theoretically remove all particle sizes. Except for structures maintained by van der Waals forces only, the drag forces necessary to remove all particle dimensions and types has no impact on lines. Finally for aspect ratio up to 2, the limitation of the processes like high velocity spray is more due to the non-accessibility to the particles hidden by the structure relief rather than pattern destruction. Shock waves necessary to remove critical particles have much more stronger effects on microstructures. Therefore, acoustic or droplet jet cleanings have therefore to be carefully adjusted to remove selectively the particles. This could be achieved using a simultaneous under-etching of one mono-layer, able to lower the van der Waals interactions.

Knowing the forces of adhesion of an actual microstructure and substrate case, the general method proposed in this paper for the 2 extreme cases of the forces of adhesion of microstructures can be applied to calculate more accurately the technological node and aspect ratio thresholds for microstructure damages.

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Electrochemical Society Proceedings Volume 2003-26

EVALUATION OF MEGASONIC CLEANING PROCESSES

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ABSTRACT

To get an insight in the interaction of acoustic waves and an aqueous based cleaning chemistry, different monitoring tools were developed and the results compared to particle removal tests. A first tool is designed to capture sonoluminescence, coming from cavitation generated in the acoustic field. It will be shown that cavitation plays a central role in the particle removal. Different parameters as gas content, power and presence of surfactants are studied in relation to sonoluminescence. A second tool, based on a hydrophone, provides a detailed map of the power distribution of the acoustic waves in a cleaning tank. Diffraction patterns in the near field and attenuation profiles in the far field are extracted and the impact of bubbles to the dispersion of the acoustic power is studied.

INTRODUCTION

Driven by the need to remove smaller particles from the different substrates used in the semiconductor industry [1], efforts are made to get an insight in the chemical and physical phenomena playing a role in the particle removal [2, 3]. In megasonic cleaning processes, the understanding of these phenomena is necessary to design a clean able to remove sub 100nm particles and to prevent damage. In the literature there is so far, no common agreement on the mechanisms taking place during a megasonic cleaning process resulting in particle removal. The proposed mechanisms vary from Schlichting streaming, pressure gradients to cavitation [4, 5]. In this paper we have studied specifically the role of cavitation in the particle removal efficiency by sonoluminescence and the acoustic power distribution with a hydrophone set-up. The combination of the results of these two techniques with the particle removal, measured by light scattering, has been used to reveal partially the phenomena, taking place in the megasonic cleaning tank.

EXPERIMENTAL SET UP

Two different megasonic tools are introduced in this study, both using flat transducer arrays. The first one is an open quartz tank (PCT, Model TTF20M-360) equipped with 2 arrays of 4 transducers (26mm x 165mm), all mounted at the bottom of the tank (Max 7W/cm² at about 726kHz). The second one is a narrow single wafer quartz tank, built on a Sonosys transducer (25.4mm x 221mm), operating at a frequency of 1MHz and a variable power (Max 10W/cm²). Both tanks are supplied with degassed (Hoechst Liquicel membrane contactors) ultra pure water at flow rates from 0-10 l/min (single use). The water can be spiked at the point of use with chemicals, e.g. surfactants (concentration around the critical micelle concentration). The integration of a Mykrolis PhasorTM allows adding, in a more controlled way, different gases. In all the tests, described in this paper,

Electrochemical Society Proceedings Volume 2003-26

oxygen is added ranging from 2-40ppm, measured with an oxygen sensor (Orbisphere 3600), 3cm under the water level. A schematic overview is given in figure 1.

Each cleaning tank can be equipped with a piezoelectric hydrophone (SEA SPRH-S-1000). This device can execute a vertical motion (mounted on a motor), and is connected to a Tektronix 2430a oscilloscope that is in turn connected to a PC. The final signal that is processed and logged, is the root mean square (RMS) of the sinusoidal pressure wave present in the tank. By moving the hydrophone vertically and logging the data, this method allows us to map quickly and efficiently the acoustic power distribution in the megasonic tank system.

A set-up is built to capture the sonoluminescence signal of a defined tank system, in order to quantify cavitation. The tank can be surrounded with an optical system: a concave mirror (diameter of 259mm) in combination with a photomultiplier tube (Hamamatsu, R-980 PMT), as shown in figure 2. The PMT is a head on type with a window of 38mm in diameter and a spectral response situated in the UV spectrum, similar to the emission spectrum of a cavitating bubble [6]. During these measurements, the tank is placed in a closed box to reduce the background signal. No wafers are present in the tank during the measurements.

The particle removal efficiency is evaluated by using a light scattering tool, the KLA-Tencor SP1^{DLS}. Silicon wafers, after receiving an O₃-last IMEC cleanTM, were contaminated with SiO₂ particles, ranging from 35 to 1000nm, using an immersion-based controlled contamination procedure. All particles smaller than 50nm, lower detection limit of the SP1^{DLS}, are evaluated in the haze signal [7]. The added haze on the wafer is proportionally to the particle density starting from approximately $3x10^6$ particles/cm². Bigger particles, with a size from 150 up to 1000nm, are evaluated as individual resolved light point defects. Each wafer-cleaning test is followed by a rinse in an overflow rinse tank (3-5min) and a Marangoni dry (10min).

ACOUSTIC POWER DISTRIBUTION

The acoustic power distribution, experimentally determined from bottom to top in the single wafer tank system, is given in figure 3. A scan, in the center of the transducer is done for degassed (<30ppb O_2) and oxygen saturated (>32ppm O_2) conditions. The saturation leads, visually observed, to the presence of bubbles in the liquid.

For saturated conditions, strong attenuation is observed. The acoustic pressure starts to drop tremendously from 5cm above to the transducer, due to the presence of the sound scattering bubbles. Degassed water results in a more uniform distribution of the power in the tank. As shown in figure 3, the region close to the transducer is characterized by rapidly alternating interference maxima and minima. These effects, not observed further from the transducer, are due to the specific dimensions of the transducer and small phase shifts. The regions are respectively called near-field (Fresnel zone) and far-field (Fraunhofer zone) [12]. The transition between these zones, related to the dimensions of the transducer, is experimentally observed around 16cm and calculated at 12cm (calculations done for a similar circular piston: a^2/λ , a is the radius of the piston and λ the wavelength of the sound beam) and is known as the Fresnel focal length [12]. It can be concluded that the acoustic pressure measured in the cleaning tank is related to the non-

162

linearity of the propagating medium. In addition to diffraction and attenuation in the medium, the presence of bubbles has also a role in the dispersion of the sound beam [11].

Looking at the particle removal maps (figure 4), it can observed that the PRE drops in the Fresnel zone. A more detailed study is required focusing on the transducer design, transverse intensity distributions, bubble activities, degassing effects, etc. Rotating the wafer or moving the transducer systems, as done in single wafer cleaning, can in these cases improve the removal efficiency.

SONOLUMINESCENCE

Ultrasonic and megasonic power in liquids provide a unique environment for different physical and chemical phenomena [13]. One of the phenomena is the bubble expansion in a negative pressure cycle followed by a violent collapse, i.e. transient cavitation. The hot spot model [14] predicts high temperature in the collapsing bubble accompanied with the generation of, among others, OH and H-radicals. The recombination of these radicals into H_2O causes light emission, called *sonoluminescence*, was observed for the first time in 1934 [15]. The light measured with the sonoluminescence set up can be used as a measure for cavitation.

When 18ppm oxygen is dissolved in the liquid and introduced in a 1MHz megasonic field, as shown in figure 5, a significant sonoluminescence signal is observed. In the absence of gas (degassed conditions, <30ppb O₂), only a very small signal can be observed. Out of these results, it can be concluded that the presence of dissolved gas enhances the generation of cavitation. All the tests shown here are done in single pass mode at flow rates of 61/min. This explains the constant sonoluminescence signal over time. When the transducers are switched on (after 5 seconds), a spike in the signal is observed indicating a higher bubble activity at the start of the process. By switching off the transducer (after 50 sec) the signal level will drop immediately to the background signal of the photomultiplier.

Different sizes of SiO₂-particles were evaluated for particle removal efficiency in the PCT tank. Two different conditions (cfr. Sonoluminescence test), gasified and degassed ultra pure water (single pass, 10l/min) for a 5min megasonic process, were evaluated next to the reference (only a flow of ultra pure water, no megasonics, and a Marangoni dry). As shown in figure 6, it can be observed that the presence of gas is required to achieve reasonable cleaning results for all particle sizes. These results confirm that cavitation [8] is the main cleaning mechanism. In the cases of cleaning in a degassed environment (<<500ppb, traces of oxygen present due to the open overflow tank system), we can observe that no particle removal is obtained for particles smaller than 200nm. The bigger particles are partially removed by the rinse and Marangoni based dry on one hand and by streaming effects close to the boundary layer (Schlichting streaming [9]) on the other hand. The decreasing particle removal efficiency for decreasing particle size tested, is due to the non-uniformity of the cleaning mechanism [10].

Experimental results on particle removal efficiency indicate also the importance of dissolved gas in SC1 mixtures [10].

Experimentally is a clear one-to-one relationship between power, cavitation and removal efficiency (figure 7) for sub-100nm particles observed. Dealing with higher power

Electrochemical Society Proceedings Volume 2003-26

settings, more cavitation seeds will exceed their cavitation threshold [14], and form a collapsing bubble.

In the fine-tuning of the megasonic process, the gas content plays an important role. In figure 8 an optimum can be found in the lower gas concentration region. This explains the particle removal data in figure 9. The observation can be linked to the dispersion of the sound beam by the presence of bubbles in the liquid.

The introduction of surfactants in megasonic cleaning is done to have better wetting conditions and an influence on the surface charge of wafer and particles. But it leads also to a lower surface tension and the presence of more cavitation seeds. The influence of gas concentration and surfactants is given in figure 10. For high gas concentrations no significant difference is observed in the sonoluminescence signal, but for lower gas concentrations the role of the surfactants is more considerable. In completely degassed conditions, saturation in the sonoluminescence signal is observed. Referring to the particle removal data, it can be concluded that the increase of the sonoluminescence signal is not only due to a more intensive generation of radicals but also to a higher cavitation activity. These data give us the opportunity to define a good process window for the megasonic tank systems.

CONCLUSIONS

It can be concluded that the particle removal efficiency is related to sonoluminescence, indicating that cavitation is the main cleaning mechanism in a megasonic tank system. Through the construction of a sonoluminescence set up, the role of different parameters as gas content, power and the presence of chemicals could be determined quantitatively. This allows us to define better process windows for particle removal in a megasonic tank system. The quick and accurate mapping of the power distribution, showed us the near field effects (diffraction) and far field effects (attenuation) and that the presence of bubbles plays a role in the dispersion of the sound beam.

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Electrochemical Society Proceedings Volume 2003-26

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Fig. 1: Experimental set up used in the different tests: degassing, O₂ gasification and spiking of surfactants in a single pass mode ...



set-up.

Fig. 3: Intensity of the acoustic wave in a degassed and gas saturated tank.

Electrochemical Society Proceedings Volume 2003-26



Fig. 4: Particle removal plot (SP1): the upper part has a high particle removal and the lower part low particle removal efficiency.



Fig. 6: Particle removal efficiency evaluated in megasonic cleaning tank, for different sizes of SiO₂-particles in different conditions of the ultra pure water: degassed, gasified and no megasonics (reference).



Fig. 5: Sonoluminescence measured for a 50 sec megasonic process (switched on after 5 seconds). The two conditions are a 18ppm O2 solution and a degassed solutions (<30ppb).



Fig. 7: Sonoluminescence and particle removal ($30nm SiO_2$ particles) measured for different power settings of the generator.

Electrochemical Society Proceedings Volume 2003-26



Fig. 8: Sonoluminescence measured for



Fig. 10: Sonoluminescence measured for different gas and surfactant settings at 90%



Fig. 9: Particle removal data for 30nm SiO₂ for different O₂ concentrations.



Fig. 11: Particle removal data for 30nm SiO₂ for different gas and surfactants settings.

Electrochemical Society Proceedings Volume 2003-26

STUDY OF THE CLEANING CONTROL USING A MEGAHERTZ NOZZLE SOUND PRESSURE MONITOR SYSTEM FOR SINGLE-PLATE SPIN CLEANERS

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ABSTRACT

We have developed a sound pressure monitoring system for a single-plate spin cleaner, in order to measure and control the sound pressure of a megahertz-band (MHz-band) nozzle. In this cleaning system, a single-plate cleaner is used for removing particles in the wet cleaning processes of manufacturing semiconductor devices. However, the damage to aluminum (Al) wirings due to the ultrasonic nozzle (MHz nozzle) of oscillation frequencies around 1.5 MHz has not yet been clarified. The developed sound pressure monitoring system has improved symmetrical angle characteristics for receiving sound waves, relative to a central axis, due to the modified sensor configuration and measurement error of less than $\pm 2\%$. High chemical resistance was also achieved by using a quartz and fluoroethylene plastic vessel. These designs have led to a good understanding of the dependence of sound pressure behavior on the liquid flow rate and dissolved gas concentration.

INTRODUCTION

In the manufacturing processes of semiconductor devices, megahertz-band (MHz-band) ultrasonic cleaning is widely used for the removal of submicron particles from silicon (Si) wafers. The ultrasonic wave of the MHz-band has been believed to be nondamaging to semiconductor devices, since this system does not generate cavitation in the liquid (1). However, we have observed the induction of cavitation by MHz-band ultrasonic waves, as well as crack generation in Si wafers (2)(3). Damage to aluminum (Al) wiring with a line width of 0.5 µm has also been reported (4). In order to remove submicron particles without damage, sound pressure control of a megahertz nozzle (MHz nozzle) is needed since damage is induced by the high sound pressure of ultrasonic waves (5).

A variety of spin-type process equipment is used in the single-plate cleaner in semiconductor device manufacturing. The ultrasonic nozzle with oscillation
frequencies of approximately 1.5 MHz is used for these MHz cleaning units. In order to measure and control the sound pressure in the MHz nozzle, it is required to optimize the sound pressure sensor and nozzle angle. These optimizations can reduce the fluctuation of measured values, since the angle characteristics of receiving sound waves for the sound pressure sensor are one of the most important issues.

Therefore, we have developed a MHz nozzle sound pressure monitoring system that can be easily installed in a single-plate spin cleaner. The use of this system enables the reduction of fluctuations in measurement and high chemical resistance. Using this system, we investigated the dependence of cleaning performance on sound pressure.

EXPERIMENTAL

Figure 1 shows the sound pressure monitoring system which consists of a sound pressure sensor, a monitor, and personal computer. The face block of the sensor, which receives sound waves, was made of quartz, and the body of the sound pressure sensor was made of fluoroethylene plastic, in order to prevent metal contamination in the cleaning processes and to improve chemical resistance. The piezoelectric device, which converts sound wave pressure to electric signals, is attached at the bottom of the face block. A cylindrical top 20 mm in diameter with a spherical form is attached to the back surface. This spherical device has high performance in investigating the angle characteristics for receiving sound waves and in reducing the measurement error with high stability. This system also achieves smooth discharge of the liquid injected by a MHz nozzle toward the sensor. The electrical signals are displayed on the personal computer (PC) monitor. The monitoring system is capable of full-wave rectification of the signal wave from a sound pressure sensor, A/D conversion in an integrated circuit, and DC voltage measurement. Maximum and average data are displayed as voltage values for each sampling. Obtained by calculation during a definite time period. The PC has the functions of external control, data output, and storage. The sound pressure measurement values are continuously stored in the PC. Although this sound pressure monitoring system measures the relative sound pressure difference, it omits the absolute value correction. The voltage values from the sound pressure monitor were used as the measurement unit.

The sound pressure sensing system for a single-plate spin cleaner is shown in Fig.2. A sound pressure sensor is installed at the standby position of the MHz nozzle outside the processing cup. The sound pressure is measured during liquid purging before wafer cleaning, in order to check the possible range of sound pressure for measurement.

The diagram of the total system for gas dissolution, sound pressure sensing, and data analysis is shown in Fig.3. A vibrator with an oscillation frequency of 1.6 MHz, which is equipped in the MHz nozzle, is located at the bottom of a liquid bath filled with a deionized (DI) water with residual dissolved gas concentration of less than

169

2 ppm. This DI water is used as a propagation medium to evaluate the characteristics of the sound pressure monitoring system. The distance between the vibrator and sound pressure sensor was set at 100 mm. The sound pressure relative to the oscillation output from the vibrator, sound pressure according to the sound receiving angle, and stability in long-time operation were evaluated. The same evaluation using a commercial sound pressure monitor system for MHz nozzles was simultaneously carried out, and characteristics were compared. The relationship among sound pressure, discharge flow rate and dissolved gas concentration was investigated using two kinds of MHz nozzles in the sound pressure monitoring system. The flow rate of DI water with dissolved gas concentrations of 2 ppm or less was 1.2 to 1.6 ℓ /min. The distance between the nozzle and the sound pressure sensor was maintained at 30 mm. In the evaluation of the effect of changing the dissolved gas concentration in DI water was set at 1.3 5 or 50 ppm.



Fig.1 Sound pressure monitoring system.



Fig.2 The sound pressure sensing system for a single-plate spin cleaner.

170



Fig.3 The diagram for characterization of sound pressure sensor.

RESULT & DISCUSSION

The sensitivities of sound pressure measurements using a commercial sound pressure monitoring system (A) and the developed sound pressure monitoring system (B) on sound receiving angle are shown in Fig.4. The angle characteristics of receiving sound waves including stability were determined by optimizing the face block form. The sensitivity of the sound pressure monitoring system (A) changes depending on the angle it was very low at the receiving angle of 0 degree and maximum at 25 degrees. On the other hand, the maximum sensitivity of the developed sound pressure monitoring system (B) was observed at a receiving angle of 0 degree. The sensitivity was symmetrical at the angle of 0 degree. This symmetrical characteristic can reduce the measurement error in the sound pressure monitoring system.

Figure 5 shows the relationship between the sound pressure and oscillation output. Because the time constant of measurement is large, the data obtained using a commercial sound pressure monitoring system (A) are actual values. Therefore, the difference due to an oscillation wave is not apparent. As for the actual values measured using the developed sound pressure monitoring system (B), an oscillation wave becomes almost the same amplitude-modulation wave (AM wave) as a sine wave. Since the maximum value of sound pressure for the AM wave is about 35 % higher than the actual value, the feature of oscillation wave is accurately detected.

Figure 6 shows the stability during long-time operation. A step change was observed in the commercial sound pressure monitoring system (A), and the standard deviation/average was 0.041. On the other hand, the standard deviation/average for the developed sound pressure monitoring system (B) was 0.014, indicating a very small error of less than 2%. These results show that the developed sound pressure monitoring system has better characteristics than the commercial sound pressure monitoring system. Therefore, we believe that the developed sound pressure monitoring system has sufficient controllability of sound pressure of MHz nozzle.



Fig.4 The sensitivity of the sound receiving angle.



Fig.5 The relationship between the sound pressure and oscillation output.

172



Fig.6 Stability during long-time operation.

Next, the evaluation results of the characteristics of the MHz nozzle using this sound pressure monitoring system is described. We evaluated the characteristics of two kinds of MHz nozzles, made by different manufacturers, for sound pressure monitoring systems. The sound pressures relative to the oscillation output at discharge flow rates of 1.2, 1.4, and 1.6 ℓ /min in the MHz nozzle were measured. Figure 7 shows the experimental results. Nozzle (A) shows a small change in the sound pressure with flow rate change, however, the sound pressure for nozzle (B) was high at a low flow rate and low oscillation output. It then markedly decreased at a high oscillation output. This may be due to turbulent flow propagation in nozzle (B) with increasing flow rate. Since the sound waves that distribute liquid inside a nozzle are disrupted due to the scattering of liquid, the attenuation of sound pressure increases. It is considered that liquid scattering promotes atomization at a high oscillation output, leading to a sharp decrease in sound pressure.

The evaluation results of characteristics in terms of dissolved gas concentration are shown in Fig.8. The sound pressure value relative to each oscillation output is shown, where the dissolved oxygen concentrations in DI water was set at 1, 35 or 50 ppm. For nozzle (A), sound pressure markedly decreased with increasing dissolved oxygen concentration. On the other hand, although the relative sound pressure changed for nozzle (B) at low oscillation output, no significant difference arose at high oscillation output. It is considered that this difference was due to the difference in the liquid flow in the nozzle, indicating that nozzle (A) may suppress the generation of turbulent flow in the nozzle. This means that the nozzle (A) has exhibits rectification characteristics. Therefore, although the sound pressure change due to flow rate change can be controlled, discharge of air bubbles degrades when the liquids easily include and/or generate air bubbles. The increase in dissolved gas concentration also affects the discharge of air bubbles. The decrease in sound pressure is due to the reflection and

173

absorption of sound at bubbles. However in nozzle (B), air bubbles included in the liquid flow due to the turbulent flow are easily discharged. Therefore, it is considered that a decrease in sound pressure does not occur even when dissolved gas concentration increases.

The evaluation of the characteristics of the MHz nozzle using our new sound pressure monitoring system can clarify the sound pressure characteristics of each nozzle. This means that this sound pressure monitoring system has high capability to adjust and control sound pressure to be optimum for the processes using ultrasonic devices. Furthermore, pattern-dependent damage to Al wirings by the MHz nozzle can be characterized in detail. Therefore, it is effective to develop a damage-free wet cleaning process with high performance for particle removal.



Fig.7 The sound pressure to the oscillation output as varying discharge flow rates.



Fig.8 The sound pressure to the oscillation output as varying dissolved oxygen concentration in DIW.

174

CONCLUTIONS

We developed a sound pressure monitoring system for MHz nozzles that can be easily installed in a single-plate spin cleaner. This system has improved receiving angle characteristics of sounds and stability. By adopting a chemically resistant component for the bath, the sensor can be used for ozonized water.

The sound pressures for two kinds of MHz nozzles were evaluated using the developed sound pressure monitoring system. The behavior of the change in sound pressure with discharge flow rate and dissolved gas concentration was clarified.

In conclusion, we can develop and control accurate cleaning conditions for various device fabrication processes, using the developed sound pressure monitoring system.

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EXPERIMENTAL VALIDATION OF A SCIENCE-BASED UNDERCUT REMOVAL MODEL FOR THE CLEANING OF MICRON SCALE PARTICLES FROM SURFACES

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ABSTRACT

A theoretical model for undercut removal of particles from surfaces is proposed on the basis of forces acting on the adhering particle. The model describes adhesive interactions for particles on surfaces based on computer simulation of van der Waals and electrostatic double layer forces during substrate etching. Undercut removal of polystyrene latex spheres adhering to tetraethyl ortho-silicate - sourced silicon dioxide was examined as a function of etch time in 20:1 buffered hydrofluoric acid. Experimental results for 7 and 15 μ m PSL particles were consistent with model predictions for etch times of 60 and 105s.

Key-words: particle adhesion, particle removal, van der Waals force, electrostatic double layer force, etch kinetics, undercut cleaning, post-CMP cleaning

INTRODUCTION

Wafer cleaning is an important step in semiconductor processing since it serves to remove particulate contaminants adhering to wafer surfaces. Cleaning of wafer surfaces during semiconductor processing is achieved through wet and dry cleaning methods. Wet methods generally involve hydrodynamic removal, chemical etching or a combination of both. In this paper we report on the undercut removal of micron-scale particles from wafer surfaces in non-flow systems. Particle removal was studied as a function of immersion time in an etch bath containing 20:1 buffered hydrofluoric acid (BHF). A model for the description of undercut removal was proposed. The model assumes that undercut cleaning occurs when the regions of close particle-substrate separation are reduced by the etching process. This reduces the magnitude of attractive van der Waals (VDW) interactions and allows repulsive electrostatic interactions to become dominant. The removal criterion for the adhering particle is based on a balance of these forces. As the magnitude of the electrostatic force becomes comparable to that of the VDW force, the system reaches a stage where the total VDW force is less than that of the total electrostatic double layer force, and particles are removed from the surface.

Electrochemical Society Proceedings Volume 2003-26

THEORY

The model system consists of a rough deformable particle adhering to a rough surface. Figure 1 is a schematic representation of the system under stagnant conditions before the undercut process. The forces acting on the adhering particle are the VDW force of adhesion and the electrostatic double-layer force (EDL). The net force of adhesion can be approximated as the sum of the VDW and EDL forces as described by Eq. 1 (1).

$$\overline{F_A} = \overline{F_{vd}} + \overline{F_E} \tag{1}$$

The particle sits on the surface with a separation distance h_0 , which is assumed to be the Lennard-Jones separation distance. The region of particle-surface contact is assumed to be circular with a radius a_0 .



Figure 1. Schematic diagram of the model system

The total VDW force, $\overline{F_{vd}}$ for a smooth deformable particle adhering to a smooth surface is given by:

$$\overline{F_{vd}} = \frac{Ad}{12h^2} \left[1 + \frac{2a^2}{hd} \right]$$
(2)

177

where A is the Hamaker constant, h is the particle-surface separation distance in contact, d is the particle diameter and a is the contact radius due to deformation of the particle. The Hamaker constant (A) is dependent on the composition of the particle, surface and medium (2). A was computed using atomic force microscopy measurements (AFM) of PSL interacting with silica and fitting the first term of Eq. 2 to the data (3). The contact radius was estimated using theory developed by Johnson, Kendall and Roberts (4-6). The system under consideration is different from the ideal case that Eq. 2 describes, since the particle and surface have finite roughness distributions. The roughness causes a significant difference between computed adhesion force using Eq. 2 and measured forces (7, 8). A modified computational scheme described by Cooper, was used to estimate F_{vd} .

The model used accounted for particle and surface roughness distributions by creating roughness distributions on model surfaces with the same mean and standard deviation in roughness as that of the actual particle-surface system.

The EDL force ($\overline{F_E}$) is (9):

$$\overline{F}_{E} = \frac{\varepsilon\varepsilon_{0}d}{4} \frac{\kappa e^{-\kappa h}}{1 - e^{-2\kappa h}} \left(\psi_{p}^{2} + \psi_{s}^{2}\right) \left| \frac{2\psi_{p}\psi_{s}}{\psi_{p}^{2} + \psi_{s}^{2}} - e^{-\kappa h} \right|$$
(3)

where, ε is the dielectric constant of the medium, ε_0 is the permittivity of free space, ψ_p and ψ_s are the particle and surface potentials and κ is the reciprocal double layer thickness. The value of ψ_p is approximated by the particle zeta potential while the value of ψ_s is approximated by the surface zeta potential (computed using streaming potential measurements for the surface). In general, since the particle and surface zeta potentials are functions of the pH of the medium, the magnitude and sign of $\overline{F_E}$ changes as the pH of the medium changes (10-15). The value of F_E was computed by integrating Eq. 3 over the etch profile created by isotropic etching of the substrate.

The values of F_{vd} and F_E need to be determined as a function of time during the undercut process. In the current study, BHF is used to etch silica, which results in an isotropic etch profile. The etching of the surface occurs in a large excess of etching medium and is assumed to be free from mass transport limitations, such that the rate of the etching is assumed to be constant. The etch rate is a function of the concentrations of the primary etching species in the medium. Therefore, these need to be identified before suggesting a mechanism for the etching (16, 17).

For the given system, F_{vd} is always attractive and F_E is repulsive. Figure 2 is a schematic of the etch profile at an intermediate time during the etch process. The total EDL force was computed using Eq. 4 to integrate over the etch profile.

$$F_{E,iotal}\Big|_{t} = F_{E,deform}\Big|_{t} + \int_{a}^{b} F_{E}(h(x)\Big|_{t})dx$$

$$\tag{4}$$



Figure 2. Schematic diagram of the etch profile

Electrochemical Society Proceedings Volume 2003-26

Particle removal is dependent on the magnitude of the net adhesion force described by Eq. 1. To cause the complete removal of a given particle from a surface, the magnitude of the adhesion force should be zero or repulsive (negative sign). This occurs when the magnitude of the repulsive total EDL force is equal to or greater than the total VDW force.

EXPERIMENTAL

Etching experiments were performed using coupons cleaved from a silicon wafer with a tetra ethyl ortho silicate (TEOS)-sourced silicon dioxide surface layer that was ~10,000 Å thick. The etching medium used was 20:1 buffered hydrofluoric acid (BHF). Undercut removal of PSL particles from the silicon dioxide surfaces was studied under non-flow conditions. Optical ellipsometry was used to determine film thickness of the oxide at various stages during the etch process. The etch rate of the oxide in 20:1 BHF was found to be 31 nm/min.

The particle sizes used were 7 and 15 μ m and were purchased from Duke Scientific in the form of a concentrated suspension. The suspensions were diluted and subsequently spray deposited onto 200 mm TEOS-sourced oxide wafers. The particles were allowed to settle for 24 hrs to allow elastic deformation. The wafers were etched using 20:1 BHF for varying lengths of time and subsequently immersed in a water bath to stop the etching. Pre- and post-etch scans of the wafer surface were obtained using a Tencor Surfscan SP1 system. Particle counts for the pre and post-etch scans were used to determine the percent of particles adhering to the surface after the given length of the etch process.

RESULTS

The undercut removal model was evaluated for etch times of 60 and 105 s using the equilibrium contact areas computed by the JKR model (4-6). The equilibrium contact area for 7 μ m PSL particles computed using JKR theory is about 95 nm and that for 15 μ m particles is 159 nm. Undercut removal of equilibrated PSL spheres was studied using 20:1 BHF solution to undercut the silicon dioxide surface. Two replicates of the removal experiments were carried out for each particle size for immersion times of 60 and 105 s. The results of these experiments are shown in Figure 3. The undercut model (Eq. 1) was used to predict the percentage of particles removed for etch times of 60 and 105 s. simulation results have also been displayed in Figure 3.

Electrochemical Society Proceedings Volume 2003-26



Figure 3. Percent of particles adhering to oxide surface for (a) 15 µm PSL (b) 7 µm PSL

The error bars on the experimental data points represent error in measurement of percentage of particles adhering. The error bars on the simulation data points represent a $\pm 10\%$ range in calculated contact areas. These bounds represent two possible causes for variation in computed contact area. The upper bound denotes the case where the particles failed to achieve equilibrium deformation. The lower bound addresses the possibility that the JKR theory under-predicts the contact area. From Figure 3, it is seen that the experimental data lie within the $\pm 10\%$ of the model prediction.

It was found that a larger percentage of the 15 μ m particles remain adhered to the surface than 7 μ m particles for a given etch time. This was attributed to the fact that the contact area for 15 μ m particles is larger than that for 7 μ m particles. A larger contact area results in a larger VDW force of adhesion leading to which requires more undercut before particles can be removed.

CONCLUSIONS

Removal of micron-scale particles was studied for a system consisting of PSL particles on a TEOS-sourced silicon dioxide surface. The surface was etched using 20:1 BHF solution and particles were removed due to undercutting of the substrate. Experimental and theoretical predictions for particle removal were found to agree within 10%. The proposed undercut removal model provided a reasonable first generation estimate of the behavior of micron-scale PSL spheres adhering to the silicon dioxide surface.

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Electrochemical Society Proceedings Volume 2003-26

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Electrochemical Society Proceedings Volume 2003-26

Resonance Damage of Semiconductors by Acoustic Excitation

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ABSTRACT

There are many theories for the mechanism of damage to fine polysilicon gate features during cleaning with Megasonic energy. Resonate excitation, the destruction of a feature by acoustically driving the feature at a natural vibrational mode, has often been proposed. This work analyzes the natural resonant frequencies of typical polysilicon gate lines using both finite-element analysis and with an analytic solution from classical mechanical engineering. The calculated values are then compared to the frequencies present in megasonic cleaning baths. The resonant frequencies of more compliant materials such as SiO₂, metals and organic dielectrics are also discussed.

INTRODUCTION

Megasonic energy, sound in the megahertz frequency range, has been used for many years in cleaning semiconductors. Higher frequency excitation was chosen after it was discovered that ultrasonic cleaners (20 to 100 khz) were damaging features on the wafers. The damage mechanism has not been positively identified, and damage may occur by more than one mechanism.

One often proposed mechanism for damage involves acoustic resonance.[1] Damage by acoustic resonance can occur when a mechanical structure is exposed to vibrations with frequency content near a resonant frequency of the structure. Each vibrational mode, with its particular shape of deformation of a structure, corresponds to a single frequency.

Exposed lines on an in-process integrated circuit can be modeled as cantilever beams to determine their response to vibration. The shape of the first three, 2-dimensional vibrational modes of a cantilever beam are shown in Figure 1.[†] Mode 1 has the lowest resonant frequency, with the frequency of other modes increasing with mode number. In general, the frequency of a mode increases as the radius of bending necessary to form the mode decreases.

In this paper we model the vibration response of polysilicon lines both analytically and by finite element analysis. The predicted resonances are compared with the power spectra of a typical megasonic unit. Finally, the resonant frequencies of SiO₂, metal and organic dielectric lines are discussed.

[†] In a 2-dimensional mode, bending is assumed to occur only along the height of the line, and occurs uniformly along the length of the line. I.e., elements along the whole length of the line bend back-and-forth in unison.





ANALYTICAL SOLUTION

The analytical solution to determine the normal modes and natural frequencies of a 2dimensional cantilever (also known as a clamped-free beam) are given by Meirovitch.[2] The general solution for the natural resonant frequencies of a cantilever is:

$$f_i = \frac{\lambda_i^2}{2\pi h^2} \left(\frac{EI}{m}\right)^{1/2}$$
[1]

Where i is the vibrational mode number, E is young's modulus (170 GPa for polysilicon), I is the area moment of the beam, h is the span of the beam (the feature height) and m is the beam's mass per unit length. Values for λ_i are dictated by the boundary conditions and are shown in Table 1.

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Mode	λ_i	$f_{\rm i}({\rm MHz})$	$f_{\rm i}$ (MHz)		
		0.05 x 0.15	0.1 x 0.45		
		μm	μm		
1	1.875	3,066	681		
2	4.694	19,216	4,268		
3	7.855	53,810	11,952		

Table 1: λ_i and resonate frequencies for the first three vibrational modes for typical polysilicon line geometries.

The area moment I is given by:

$$I = \frac{1}{12} L w^3$$
 [2]

where L is the length of the line w is the line width. Simplifying:

$$f_i = \frac{\lambda_i^2 w}{2\pi h^2} \left(\frac{E}{12\rho}\right)^{1/2}$$
[3]

Electrochemical Society Proceedings Volume 2003-26

where ρ is the density of polysilicon (2.33 g/cm³). The resonant frequency of these 2dimensional modes are independent of line length, proportional to line width and inversely proportional to the line's height squared. For shrinking lines with a constant aspect ratio, the resonant frequency increases as 1/width as the line width decreases. The shapes of the first three, 2-dimensional modes are shown in Figure 1.

Table 1 shows the resonant frequencies of the first three modes for two line geometries. The lowest resonant frequency listed is near 700 MHz, far above the 1 MHz used in cleaning applications. Figure 2 shows a graph of resonant frequency vs line height for various line widths. A 25 nm wide line would have to be nearly 6 microns high, a 400:1 aspect ratio, to resonate near 1 MHz. These analytic calculations indicate that there is no danger of damage to poly gate structures by the resonance mechanism.



Figure 2: Resonant frequencies of the first order vibrational mode for polysilicon lines.

The resonant frequency for a given structure scales by the material's properties as $(Young's modulus/density)^{1/2}$. Table 2 shows the scaling factors for common semiconductor materials. The resonant frequency for a structure of a particular material can be determined by multiplying the frequency shown in Figure 2 by the scaling factor in Table 2. Even in the extreme case of a carbon-based low-k dielectric, the resonant frequency is only reduced by a factor of 5, and resonant frequencies of typical line structures remain above 100 MHz.

There does exist, however, the potential of resonance damage to MEMS structures whose geometry lies at the lower right of Figure 2. For instance, a 1 μ m thick by 40 μ m long cantilever would resonate near 1 MHz and could easily be excited to destruction during Megasonic cleaning. The possibility of damage to MEMS with resonant frequencies below 10 MHz is possible as the harmonics and subharmonics of the 1 MHz fundamental are present while cleaning (see MEGASONIC FREQUENCY SPECTRUM below).

184

Material	Density	Young's	Frequency
	(g/cc)	Modulus	Scaling Factor
		(GPa)	
Si	2.33	170	1
SiO ₂	2.18	70	0.66
Al	2.70	70	0.60
Cu	8.92	130	0.45
SiLk tm	1.07	3.47	0.21

Table 2: Scaling factors for resonant frequencies from Figure 2 for various materials.

FINITE ELEMENT ANALYSIS

In order to confirm the analytical results, a 0.1x0.45x45 micron polysilicon line was modeled by finite element analysis using the ANSYS FEA package. The FEA model predicted the frequency of the first order, 2-dimensional mode to be 673.3 MHz, in excellent agreement with the 681 MHz predicted by the analytic model in Table 1.

The next resonant frequencies found corresponded to 3-dimensional modes where the line locally deformed as shown in mode 1 of Figure 1, but deformed in alternate directions along the length of the line. The third, 3-dimensional mode where the ends of the line bend one way and the center the opposite way is shown in Figure 3.



Figure 3: deformation pattern of the 3rd, 3-dimensional mode.

The frequencies of the first few 3-dimensional modes are shown in Table 3. The frequencies do not vary significantly from that of the first 2-dimensional mode. Therefore, the results shown in Figure 2 are still valid. Table 3 also shows the FEA results for the same line with one end fixed, simulating a corner in the line. The corner structure does not induce a significant shift in the resonant frequencies.

VISCOUS DAMPING

The above analysis are for cantilevers in a vacuum. Atomic Force Microscopy work in the life sciences has highlighted the fact that the resonant frequency of a small cantilever in a liquid decreases to $f_L/f_V \sim 0.25$ -0.3 of the vacuum value.[3] This can be

Electrochemical Society Proceedings Volume 2003-26

understood intuitively as the cantilever's mass being increased by the mass of the liquid boundary layer that travels with the cantilever in its motion.

This four-fold decrease is not sufficient to bring the resonance of sub-micron features into the low-Megahertz frequency range of megasonic cleaners. Further, the frequency shift occurs because a driven structure must "drag" the un-driven liquid. In the present case, the driven liquid drags the structure, and no frequency suppression should occur.

3-Dimensional	Mode Frequency	Mode Frequency		
Mode Number	Free Line	Line with Corner		
	(MHz)	(MHz)		
1	673.3	673.3		
2	673.4	673.6		
3	673.8	674.3		
4	674.6	675.2		
5	675.7	676.5		
6	677.2	678.1		
7	678.9	680.0		
8	680.9	682.3		

Table 3:	Resonant	frequence	cies for	the 3	-dimen	sional
modes	of a 0.1x().45x45	micron	polys	silicon l	ine.

MEGASONIC FREQUENCY SPECTRUM

There is generally power in a megasonic bath at frequencies well above the 1 MHz fundamental. Nonlinear oscillations of bubbles can create harmonics, subharmonics and superharmonics of the driving frequency with frequencies *nf*, *f*/m, *nf*/m respectively (n and m are small integers). Also, cavitation events create a background of "white noise" that covers a broad range of frequencies.

Figure 4 shows the Power Spectral Density in a typical megasonic cleaning bath operating at a fundamental frequency of 950 kHz. The sound field was sensed with an SPRH-S-1000 hydrophone (Onda Corporation) whose signal was digitized at 20 MHz by a PCIDAS4020/12 A/D board (Measurement Computing) and gathered and analyzed with the LabView software package (National Instruments). While high-frequency harmonics of the fundamental are present, the power in each harmonic drops rapidly with increasing frequency. The 5th harmonic has only 1/1,000th the power present in the fundamental. The power above 100 MHz (above the 100th harmonic), will be negligible.

EXPERIMENTAL CONFIRMATION

Further confirmation of the results of the resonance models was obtained by testing the resonance frequency of a 160 mm long by 680 μ m thick section of a 200 mm Si wafer Figure 5. The predicted frequency of 36.6 Hz compared well with the 37 Hz experimental value, confirming the theoretical analysis.

Electrochemical Society Proceedings Volume 2003-26



Figure 4: Typical Power Spectral Density of sound in a Megasonic cleaning bath. The linear scale of the x axis runs from 0 to 10 MHz.



Figure 5: Segment of 200 mm wafer used in experimental vibration tests.

OTHER DAMAGE MECHANISMS

While the above analysis is compelling, the question of the true damage mechanism remains. Figure 6 shows an SEM of a damage site on a 60x220 nm polysilicon line. Figure 7 shows an optical micrograph of multiple damage sites on dense arrays of polysilicon lines in a heavily damaged area. Each site visually appears to be 1 to 2 microns in length. The extent of all individual damage sites surveyed is quite localized, typically restricted to an area a few microns in diameter. These data indicate a localized concentration of energy incompatible with the resonance-damage theory.

On lightly damaged samples, individual damage sites are usually widely spaced and are believed to be unrelated. Occasionally, however, closely-spaced damage events occur, particularly in heavily damaged areas. For example, the four damage sites on the left side of Figure 7 appear related. Apparently, in some cases the primary damage mechanism, or some secondary mechanism, can produce multiple damage sites in a localized area.

187

Figure 8 shows damage-free arrays of 60x220 nm polysilicon lines after megasonic cleaning. The changes in process conditions between Figures 7 and 8 were all designed to control the number, size and nature of cavitation events. While some of the process condition changes could also effect other proposed damage mechanisms, it is believed that cavitation is the primary mechanism by which damage occurs to small features in megasonic cleaning.



Figure 6: SEM micrograph of damage to one of three individual 60x220 nm polysilicon lines. 2 micron horizontal field of view.



Figure 7: Optical micrograph of damage within dense arrays of 60x220 nm polysilicon lines. 90 micron horizontal field of view.



Figure 8: Optical image showing the reduction of damage to dense arrays of 60x220 nm polysilicon lines by varying factors expected to affect cavitation during the megasonic process. 135 micron horizontal field of view.

CONCLUSION

It is highly unlikely that resonant excitation plays a significant role in damage to polysilicon gate features or sub-micron scale features of other materials. Megasonics could, however, damage micron-scale MEMS devices. Cavitation is the likely damage mechanism, as the damage rate is strongly affected by process variables known to affect cavitation.

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Electrochemical Society Proceedings Volume 2003-26

Substrate Damage-free Laser Shock Cleaning of Particles

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ABSTRACT

No dry process has been able to remove inorganic particles effectively without inducing damage. Wet process, although effective, does use large amounts of water and is compatible with vacuum process. Many cleaning steps are used after dry process to remove particulate contaminants introduced during etching or thin film deposition processes. Laser cleaning has been considered by many as possible technique for the removal of particulate contaminants. However, the direct dry laser irradiation of wafers has not been shown to remove inorganic particles and could easily cause surface damage. Wet or laser cleaning has been shown to be effective in the removal of organic particles, however, it has been shown to damage patterned wafers. In this article, we introduce dry laser cleaning method using a shock wave generated just above the wafer surface. The particle removal is caused by the gas high velocity induced by the propagating shock wave.

INTRODUCTION

In semiconductor manufacturing, a wafer surface cleaning is one of the most important processes as the integration density of device increases and the higher yield without production loss is required. A well-known RCA wet cleaning chemistry has been applied in the semiconductor manufacturing conventionally. However, the strong chemicals could easily attack the sensitive surfaces such as metal interconnect and low-k materials, and the application of 300 mm wafers causes the more consumption of chemicals inducing higher cost and environment impacts. In order to tackle these problems, there have been many efforts to develop dry cleaning method [1].

In recent, laser cleaning technique has been demonstrated to be successful for the removal of particles by an environmental friendly route, since it is a dry process [2-7]. However, laser cleaning has its own disadvantages. For example, the speed of cleaning is relatively slow due to small laser spot size, and direct interactions between the laser beam and the substrate may cause severe surface damage on the delicate wafer surface. Furthermore, inorganic particles smaller than the laser wavelength is difficult to remove due to the limitation in the enhancement of cleaning force, which should be larger than adhesion force for cleaning [8]. Therefore, a more effective laser cleaning technique is required not only to obtain high throughput by high speed but also to remove the small particles successfully without inducing any damages.

Chemical mechanical polishing (CMP) is a removal process. It strips part of the deposited films by the combination of chemical reaction and mechanical polishing, thus making the surface smoother and more planarized. It is commonly used to remove bulk dielectric film on the surface to form shallow trench isolation (STI) on silicon substrate, and to remove bulk metal film from the wafer surface to form metal interconnection plugs or lines in the dielectric film. Small particles in slurry mechanically abrade the

wafer surface and remove surface materials during the CMP process. These particles should be removed after the CMP process in order to avoid any defects, thus post CMP cleaning is a critical process. Usually double-sided scrubbers are used for the post-CMP cleaning process.

In this article, a new dry cleaning methodology named 'laser-induced shock cleaning' is applied to remove very small slurry particles from post-CMP wafers in order to see the cleaning capability of the new methodology named 'laser-induced shock cleaning' is applied to remove very small slurry particles from post-CMP wafers in order to see the cleaning capability of the new methodology

Laser Induced Shockwave Plasma Cleaning

Laser-induced shock cleaning technique is a new cleaning methodology particularly for the effective removal of small particles which utilizes airborne plasma shock waves without any direct interactions between the laser beam and the surface [9-11]. When the intense laser beam is focused in the air just above the wafer surface, the gaseous constituents began to breakdown and to be ionized, producing a intense airborne plasma. Subsequently an intense shock wave is generated by the rapid expansion of the plasma and then propagates spherically toward the substrate. If the force of shock wave is larger than the adhesion force between the particle and the substrate, the particles began to detach and remove from the surface. The schematic diagram of the laser-induced shock cleaning is shown in Fig. 1

EXPERIMENTAL

A p-type (100) bare silicon wafers with the size of 4 inch supplied from LG-Siltron Co. were used. These wafers were contaminated with fumed silica particles of 14 nm in diameter. These silica particles are commonly used for oxide CMP slurry. The silica particles were deposited on silicon wafer surface by an air spray method using purified N₂ gas. A total of 3 wafers are contaminated and cleaned by laser-induced shock waves. In addition, the real patterned wafer contaminated with silica slurry after CMP process was applied to clean using the laser induced shock waves.

A Q-switched Nd:YAG laser with a wavelength of 1064 nm is used to remove the particles from the surfaces in class 1 cleanroom environment. In this experiment, the laser energy density at the focus is approximately 10¹¹ W/cm². In order to evaluate the cleaning performance, KLA-Tencor Surfscan 5500 and SEM are used before and after cleaning.

RESULTS AND DISCUSSION

In order to investigate and analyze the cleaning performance of micro and nanoscale particles quantitatively, the surface scanner was used to measure the number of particles on the surface. Also theoretical calculation of removal ratio was performed based on the shockwave velocity of 6,000 m/s. Fig. 2 shows the schematic illustration of rolling removal mechanism and brief simulation results about the shock wave cleaning. If the removal moment ratio is larger than 1 most of the particles(more than 80%) could be removed from the surface. Removal moment ratio is defined as below equations for this calculation: In order to investigate and analyze the cleaning performance quantitatively, the surface scanner was used to measure the number of particles on the surface. Fig. 3 shows the scanned images of the wafer surfaces before and after the shock cleaning process. Fig. 4 (a) shows that the silica particles are uniformly deposited on the wafer surface and a total number of particles are around 4,900 in the size of 0.1 - 10 μ m. Fig. 4 (b) shows the silicon wafer surface after laser-induced shock treatment. It is seen that most of the particles are successfully removed from the surface. Fig. 4 shows the removal

Electrochemical Society Proceedings Volume 2003-26

efficiency with particle size, which was measured by two regions, i.e. $0.2\mu m - 1.0 \mu m$, $1.0\mu m - 10\mu m$ in diameter.

The removal efficiency was defined as the ratio of the number of removed particles after cleaning to the number of total particles before cleaning, as measured by a surface scanner. Three wafers were cleaned in the same experimental condition. The average removal efficiency by laser shock cleaning was above 99 %. In addition, the removal efficiency became slightly lower at the larger particle size, i.e. about 99.7 % for 0.2-1.0 μ m, about 99.5 % for 1.0-10 μ m. This is unusual result compared to other particles such as alumina, metal in which larger particle is much easier to remove and the removal efficiency is higher at the large than the small. This is probably due to the increase of the adhesion force induced by capillary effect in the very small particle cluster. However the more detailed investigation is required in the future. From the results, it is seen that the ultra small silica particles on the silicon wafer surface were successfully removed by laser-induced shock waves.

In order to clearly understand the shock cleaning process, the removal efficiency was measured with a change in the gap distance between the laser focus and the silicon surface. Fig. 6 shows the removal efficiency as a function of the gap distance. It is shown that there was a significant decrease of the removal efficiency with an increase of the gap distance. This implies that shock force impacting the surface is strongly dependent on the distance from the shock original position. It is known that the propagating wave is attenuated exponentially with the distance (I ~ I₀ e^{-ax}). Consequently, the shock wave force decrease exponentially with the distance, the removal efficiency decreases exponentially with an increase of the gap distance.

CONCLUSIONS

In this paper, a laser-induced shock cleaning as a new dry cleaning methodology has been introduced briefly. The basic principle of this technique and characteristics of the shock wave was investigated by the visualization technique as well as by the cleaning model simulation. This is also applied to remove the very small slurry particles remained after chemical-mechanical polishing process.

A successful removal of the particles was carried out by the shock process, which has been known to be impossible to achieve it with conventional laser cleaning technique where the laser beam irradiate directly onto the surface. It is shown that the average removal efficiency is over 99 % and it is slightly dependent on the size of the particles. It is also found that the removal efficiency increases with a decrease of the gap distance between the laser focus and the surface due to the attenuation of the shock wave during propagation. Lastly it was successfully demonstrated by using a real patterned wafer that the laser-induced shock wave could remove the remaining slurry particles from a post-CMP wafer surface without any damages. As a result, laser-induced shock cleaning which is exerting enormous physical forces would be a promising technique for the removal of slurry particles from post-CMP wafers.

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Fig. 1 The schematic diagram of the laser-induced shock cleaning



Fig. 2 Rolling removal mechanism (a) and removal moment ratio(RM) (b) with a particle size at the velocity of 5 km/sec.

193



Fig. 3 The scanned images of the silicon wafer surfaces before (a) and after (b) laser-induced shock cleaning



Fig. 4 The removal efficiency of fumed silica particles from silicon wafer with particle size

Effect of Surfactants on Particle Contamination of Silicon Surface in HF Solutions

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ABSTRACT

The effect of anionic surfactants on particle adhesion in dilute HF and in subsequent DIW rinse baths has been studied. These baths were intentionally contaminated with Si_3N_4 particles. Surfactants were added in the DHF bath, only, but their impact on the particle adhesion in the contaminated subsequent DIW rinse bath was measured as well. It was found that anionic surfactants can effectively reduce particle contamination in these two baths. The effect of surfactant concentration on the contamination level was tested using three different concentrations. TXRF measurements were carried out to identify sulfur containing surfactant residues remaining on the wafer surface after DIW rinsing. Zeta-potentials of the Si_3N_4 particles in 100 ppm surfactant solutions were measured.

INTRODUCTION

HF solutions and subsequent DIW rinse may cause heavy particle contamination on silicon wafers [1,2]. Contamination level depends on both the nature and the amount of particles present in the bath. In this work the effect of surfactants on the particle adhesion has been tested.

In liquid environment both the particles and the wafer surface acquire surface charge. These charges can lead to either repulsive or attractive forces between the wafer and the particles. In oxidizing alkaline solutions silicon wafer and most of the particles portray negative surface charges. In this case the repulsive force reduces particle contamination. At low pH the magnitude of the negative surface charge is reduced or the charges may have opposite signs. Repulsive forces do not exist any more and particle contamination can take place. Surfactants in the cleaning bath may modify the surface charges on the wafer/liquid and on the particle/liquid interfaces [3]. At the same time, hydrophobic forces as well as the liquid meniscus, formed while placing the wafers into or removing them from the bath, are altered. Use of surfactants in DHF cleaning baths has been reported elsewhere [4,5]. According to these results surfactants hinder particles to redeposit after being dislodged from the surface.

Total particle contamination from HF and rinse is relevant if HF is the last cleaning step. We focus on such RCA type cleans, where DHF is followed by a particle removing SC1 step. The total number of loosely adhered particles from DHF is then not really relevant, but only a small fraction of all this contamination survives the following SC1 step, and increases the total particle count.

195

EXPERIMENT

The experiments are presented schematically in Table 1. In the test A, clean hydrophilic wafers (oxide thickness < 3 nm) were immersed in the mixture of HF/DIW and particles. Surfactant had been added in the solution before particles. After that wafers were rinsed with DIW, dried and measured. The purpose of the additional SC-1 cleaning step in the test B was to evaluate the cleaning challenge after contamination. The test C was similar to the test A except that the particles were added into the rinse tank. In each case the amount of surfactant added was 100 ppm.

The test D was performed to evaluate the effect of surfactant concentration on contamination. This test was carried out using three surfactant concentrations (1, 10 and 100 ppm).

The surfactants and their properties are presented in table 2. All these surfactants are commercially available and free of metal contamination. They are also highly watersoluble and foam only slightly during the processing. According to the theory of electrical double layer repulsion (EDR), only anionic or neutral surfactants were chosen for this experiment.

Table 1 Process tests

Table 2 Surfactants

A	В	С	D	#	Type
1. HF/DIW (1:100)	1. HF/DIW (1.100)	1. HF/DIW (1.100)	1. HE/DIW (1:100)	N1	neutral
+PARTICLES	+PARTICLES	+SURFACTANT	+SURFACTANT	A2	anionic
+SURFACTANT	+SURFACTANT	(100 ppm)	(1-100 ppm)	A3	anionic
2.	2.	DIW RINSE	DIW RINSE	A4	anionic
DIW RINSE	DIW RINSE	+PARTICLES	+PARTICLES	A5	anionic
PART.MEAS.	SC-1 CLEANING	PART.MEAS.	PART.MEAS.		
	4.		4.		
	PART.MEAS.		SC-1 CLEANING		
	·		PART.MEAS.		

The silicon nitride powder utilized in this test contains about 10 % of weight particles smaller than 0.48 μ m. Particles were mixed with small amount of DIW and they were separated using ultrasonic energy before added into the bath. The bath was then thoroughly mixed. 100 mm N-type CZ (100) polished wafers were used in these tests. Particles were measured on Censor ANS-100 laser scanning tool. The particle detection sensitivity was set to 160 nm LSE (Latex Sphere Equivalent).

Contamination experiments were also made using silicon oxide particles but silicon nitride particles were chosen for these tests. It was found during separate DIW/particle experiments, in agreement with literature reports, that silicon nitride particles tend to adhere on hydrophobic wafers more readily than silicon dioxide particles. Much larger number of SiO₂ particles than Si₃N₄ particles is needed to contaminate wafers to a fixed number of particles. That is well in line with the fact that there is only small zeta-potential difference between Si and SiO₂ in DIW. Furthermore, nitride particles are much more hydrophobic than dioxide particles.

Electrochemical Society Proceedings Volume 2003-26

All process cycles were carried out in a semi-automated wet bench. Wafers were placed in a standard PFA carrier and they were first immersed in the HF/DIW tank (volume = 8 l) for 120 s. There was no circulation in this tank and the solution was allowed settle down for 300 s before introducing the wafers. After the DHF soak the wafers were transferred promptly into the full rinse tank (volume = 8 l). The rinse step (time=240 s, four dumping cycles) was performed in an overflow type tank. Wafers were soaked for 30 s before the first dump. The SC-1 parameters were: 1:2:40 NH₄OH/H₂O₂/DIW, T = 65 °C, time = 600 s, megasonic energy 240 W (volume = 17 l). Prior to the particle measurements, wafers were spin-dried. The number of particles added without intentional contamination was less than 20.

Zeta potentials of the Si_3N_4 particles in 100 ppm surfactant solutions were measured with Coulter Delsa 440 SX in order to evaluate EDR forces (pH range 2.5–11.4). Ionic strength was kept at constant level throughout the measurements. This was done by adding ammonia (NH₃), ammonium chloride (NH₄Cl) and hydrochloride (HCl) in the mixture of DIW, surfactants and particles. Prior to the measurements, particles were separated using ultrasonic energy.

Some of the surfactants contain sulfur, and TXRF (Total Reflection X-Ray Fluorescence, Atomika 8030) measurements were carried out to evaluate the amount of these surfactants on the wafers. The surfactant residues can affect the following process steps and an additional cleaning step may be needed to remove it. Wafers were immersed in the mixture of HF/DIW/surfactant for 120 s. Measurements were made both before and after the rinse bath.

RESULTS AND DISCUSSION

Particle counts after the process tests A and B in Table 1 are presented in Figure 1. No surfactant was added in the reference baths (the last two columns in the figure). Three of the five tested surfactants were incapable of reducing particle contamination during the HF/DIW immersion. However, in the last two baths particle contamination is reduced due to the surfactants. Although surfactants can reduce the amount of contamination during the HF immersion it is also possible that the particles behave differently in the subsequent SC-1 cycle. Test B in Figure 1 shows that the SC-1 particle removal efficiency does not vary significantly with the surfactant solution. In acid solution, anionic surfactants are supposed to reduce the positive surface charge on the particle surface or it can increase the negative charge [6]. In addition, the surface charge on the wafer itself is modified. Since the force between the wafer and a particle becomes more repulsive, contamination decreases. However, the reason for the heavy contamination in the three first baths remains unclear. Wafers soaked in these baths appeared to be less hydrophobic during the withdrawal. In this case, it is possible that the heavy contamination occurred during the bath exit. A thin layer of water and particles came along with the wafers because of the surfactant layer adhered on the wafer surface. If not completely soluble with the bath, surfactant itself introduces an additional source of particle contamination. However, the number of false counts, attributed to the surfactants utilized in these tests, was estimated to be small.

Electrochemical Society Proceedings Volume 2003-26

Figure 1. Particle counts after immersion in mixture of DHF/Si₃N₄-part./surf. and DIW rinse. Left column depicts situation after contamination right and column after subsequent SC-1 step (tests A and B in table 1).



Figure 2 shows the effect of surfactants in DHF on particle contamination from rinse water (test C in Table 1). Note that there was no surfactant added intentionally into the rinse bath itself. The number of deposited particles is reduced significantly due to the protecting surfactant layer, especially for surfactants A4 and A5. Unlike in the tests A and B, surfactant A3 did not cause heavy particle deposition during the withdrawal step. In this test the amount of surfactant on the wafer surface is reduced in the rinse bath. The adhered liquid film is thinner and contains less particles. Surfactant A3 was also capable of shielding particle deposition during the contaminated bath. The reference wafers experienced no surfactant in the HF/DIW mixture.

Figure 2. Particle counts after immersion in mixture of DHF/surf. and Si_3N_4 -part. contaminated DIW rinse (test C in table 1).

198



The effect of the surfactant concentration on particle contamination is shown in figure 3. In this test only surfactant A4 was evaluated since it turned out to be the most promising candidate for contamination prevention. Half of the wafers were measured after the rinsing bath and the other half was measured after the SC-1 cleaning (test D in Table 1). No surfactant was added in the reference bath. In both cases the effect of the surfactant on the particle contamination weakens as the concentration falls. However, the number of remaining particles after the SC-1 cleaning step increases only slightly with decreasing surfactant concentration.

The TXRF measurement results for surfactant A4 are shown in figure 4. The first three values were measured on those wafers immersed only in the HF/DIW bath. Sulfur concentration decreases on the wafer surface as the surfactant concentration in the HF/DIW tank decreases. The last column in figure 4 shows the concentration of sulfur atoms after the rinse cycle. These results indicate that the surfactant was removed fairly effectively. The measured value after rinse was very close to the sulfur detection limit 3e12 at/cm² of the system, but much higher than attainable if VPD (Vapor Phase Decomposition) collection had been used. However, use of VPD was not considered

appropriate, without thorough check of recovery rate, when measuring surfactant type contamination.

Figure 3. Particle counts after immersion in mixture of DHF/surf. A4 and contaminated DIW rinse (test D in table1).



Figure 4. Sulfur surface concentration remaining after immersion in DHF/surf. A4 and after rinse. Three surfactant concentrations. After rinse result was near detection limit of 3e12 at/cm².



Figure 5 shows the zeta-potentials of the silicon nitride particles utilized in this experiment. Reference measurement was made without surfactants. Those surfactants, which hindered particle deposition effectively during the controlled contamination, managed to sustain the negative zeta-potential of the particles as the pH was lowered. On the other hand, those surfactants (N1 and A1), which caused heavy contamination in the test A and B, did not have much effect on the zeta potential in acid solution. According to these results the zeta-potential dominates particle deposition on a hydrophobic wafer surface in non-alkaline solution.

Surfactants listed on table 2 were also added in the SC-1 bath in a separate test. Both hydrophobic and hydrophilic wafers were contaminated for this test with silicon nitride and silicon dioxide particles. Figure 6 shows the removal efficiencies for given wafer surface condition and particle type for those wafers cleaned without surfactants. These surfactants had no positive effect on the true particle removal efficiency [7]. True particle removal efficiency means in this case that the wafers were measured both after the contamination and again after the SC-1 cleaning. After the second measurement, particles were identified as removed, fixed or added, based on the recorded positions and sizes in these two measurements. Both the Si_3N_4 and the SiO_2 particles were effectively removed from the hydropholic wafers. For the hydrophobic wafers, particle removal efficiency

Electrochemical Society Proceedings Volume 2003-26

drops regardless of the nature of the particles. In other words, the zeta-potential does not dominate particle removal mechanism in the SC-1. The reason for the low removal efficiency for the hydrophobic wafers is obviously the absence of a proper lift-off mechanism.





(NH3:H2O2:H2O)

Figure 6. Effect of particle type and surface condition on SC-1 cleaning efficiency. Silicon dioxide and nitride particles were used on hydrophilic and phobic surfaces.

200

CONCLUSIONS

Particle contamination in DHF solution can be reduced significantly by adding anionic surfactants in the bath. The cleaning efficiency of the subsequent SC-1 cycle remains on essentially same level. The remaining surfactant layer on the wafer surface is also capable of reducing particle contamination during the subsequent DIW rinse bath. The degree of contamination in DIW rinse depends on the surfactant concentration in the preceding DHF bath. Surfactant residues can be removed effectively by DIW rinsing. Correlation between the measured zeta-potential values in 100 ppm surfactant solution and the surfactant behavior in non-alkaline solution was found.

Silicon nitride particles stick more efficiently to hydrophobic wafer surfaces than silicon dioxide. However, after adhesion, there is little difference in removal behavior, and removal behavior is difficult for both types. On hydrophilic wafers, particle removal is adequate for both species in a single SC-1 step.

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Supercritical, Cryogenic, and Dry Cleaning

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IN-SITU PROCESS FOR PERIODIC CLEANING OF

LOW TEMPERATURE NITRIDE FURNACES

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This paper describes development of a quartz cleaning process based on thermal decomposition of NF₃. This method provides in-situ cleaning to remove loosely adherent films and thereby ensure low defect level films when using the BTBAS low temperature silicon nitride process. The cleaning method was able to successfully demonstrate consistently acceptable defect levels measured at the 0.1 μ m particle size suitable for ULSI scale device manufacturing. Etch rates were measured to identify conditions providing a short clean time, good uniformity of cleaning over the chamber with good selectivity minimizing attack of the underlying quartz furnace tube and other parts. By-product effluent gases were sampled from the tool exhaust and analyzed by FTIR and QMS giving real time data during recipe development and final process verification.

INTRODUCTION

CMOS integrated circuits are fabricated using a sequence of process steps, some of which are low-pressure chemical vapor deposition (LPCVD) of polysilicon and silicon nitride. LPCVD nitride films are typically deposited by thermally reacting DCS and NH3 at temperatures of approximately 700-750 °C. At smaller feature sizes (<0.10 μ m) advanced semiconductor devices require a reduction of thermal budget for processes involved with the sidewall spacers for the gate stack. A lower temperature method of depositing silicon nitride that is gaining favor is the use of an organic precursor [1], BTBAS (C₈H₂₂N₂Si) reacted with ammonia. However this process produces a low temperature nitride film of with high stress and can result in high particle levels on device wafers because the intrinsic stress leads to film spalling at cumulative deposit thicknesses on the quartzware of under 1 μ m.

This paper describes work to develop a robust method of providing in-situ cleaning to remove nitride films from the reactor chamber wall, wafer carrier, and other chamber parts and thereby maintain low a defect level in deposited films when using the BTBAS silicon nitride deposition process. This cleaning method was able to successfully demonstrate consistently acceptable defect levels measured at the 0.1 μ m particle size suitable for 90-nm node ULSI scale device manufacturing.

While BTBAS nitride films have a lower thermal budget (the deposition temperature is approximately 550-575 °C), the intrinsic film stress is significantly higher than for DCS films. Higher stress films require more frequent cleaning of the LPCVD furnace chamber and wafer carrier to prevent particle generation due to film spalling. LPCVD furnaces for DCS nitride are typically disassembled and wet chemical cleaned after a cumulative deposition to a thickness of

typically disassembled and wet chemical cleaned after a cumulative deposition to a thickness of approximately 20-40 μ m on the chamber walls. Because of the higher film stress, BTBAS low temperature nitride furnaces must be cleaned after a cumulative deposition of 0.25-0.35 μ m. (5 to 7 runs for 50 nm thick film depositions).

Current practice for cleaning LPCVD Si_3N_4 tubes involves cooling then removing the quartz tube from the furnace followed by wet etching with HF. The wet clean requires 8 to 16 hours of equipment downtime. The production schedule including cleaning the BTBAS nitride furnaces after every 2 days of operation would result in low system availability compared to a DCS nitride furnace that only requires cleaning after 60-90 days of production. An in-situ clean having a 2-3 hour cycle time is necessary for BTBAS nitride films to be practical in volume semiconductor manufacturing.

Previous studies [2-4] have described plasma-assisted processes for wafer pattern etching of silicon nitride using NF₃ and Benzing [5] described equipment and a process for NF₃ plasma assisted CVD chamber cleans. Other studies [5-9] have described the fundamentals of thermally activated NF₃ chamber cleans. This paper describes development of an improved chamber cleaning process based on thermal decomposition of NF₃ applied to a 200-mm large batch vertical furnace (Series 8000 AVPTM).

Etch rates were measured to identify and optimize conditions providing a short clean time, good uniformity of cleaning over the chamber with good selectivity minimizing attack of the underlying quartz furnace tube and other parts.

By-product effluent gases were sampled from the tool exhaust and analyzed by Fourier transform infrared (FTIR) Spectroscopy and Quadrapole Mass Spectrometry (QMS) giving real time data during recipe development and final process verification. Prior to each furnace clean, four batches of 100 test wafers were deposited with 50 nm of silicon nitride material leaving a combined film thickness of 200 nm to be cleaned. Clean times were reproducibly 30-32 minutes. Following the NF₃ clean, particle counts from deposited wafers through the 40 run marathon were within specifications. The baseline recipe was qualified as the thermal clean Process of Record (POR).

CANDIDATE CHEMISTRIES

Silicon nitride (SiN_x) films can be etched using a fluorine-based chemistry. SiN_x reacts with fluorine to form SiF_4 , a volatile reaction product.

$$Si_3N_4 + 12F = 3SiF_4 + 2N_2$$

Several sources of fluorine were considered: NF₃, ClF₃, and F₂. Each of these gases reacts with silicon-based materials at temperatures typical of LPCVD processing (550-600 °C). ClF₃ and F₂ are, however, highly toxic (TLV = 0.1 ppm) having LC50 values of 299 ppm and 185 ppm, respectively. NF₃, however, has an LC50 value more than 20 times higher (6,700 ppm). ClF₃ and F₂ are also corrosive on equipment metal surfaces and their supply is problematic. ClF₃

Electrochemical Society Proceedings Volume 2003-26

is limited to low volume cylinders and DOT limits transportation of F_2 to pressures <400 psig. On-site F_2 manufacturing (electrolytically from anhydrous HF and H₂) has been proposed but has issues with gas purity, particularly HF and particle contamination. Compression of F_2 is extremely hazardous and system reliability must be demonstrated. NF₃ is a convenient source of fluorine. It is unreactive under ambient conditions and readily available. Additionally, most semiconductor FABs already use NF₃ for cold wall CVD chamber cleaning and are familiar with supply and handling of this material.

ETCH RATE MEASUREMENTS

Process conditions were screened using a design of experiments methodology. Etch rates were calculated by measuring the change in thickness of thin films (SiN_x , SiO_2 , and polysilicon) deposited on silicon wafers. Film thickness was measured by ellipsometry.



Figure 1. BTBAS etch rate

Response surfaces were generated showing BTBAS nitride film etch rate variation (Fig. 1), with temperature (500-600 °C) and chamber pressure (3-80 Torr). In Figure 2, the chamber cleaning uniformity variation with pressure and NF₃ flow rates (0.5-2.0 slm) is shown. Selectivity which is the relative etch rate of the nitride film divided by thermal oxide etch rate is an indicator of resistance to overetch of the chamber and wafer carrier. Selectivity shown in Fig. 3 varied as a function of NF₃ flow rate N₂ dilution (0-10 slm), temperature and pressure.

EQUIPMENT MODIFICATIONS

Equipment modifications include an MFC (3 slm) controlled gas loop for delivery of the NF_3 with provisions for its delivery into the reactor chamber. Additional NF_3 related safety interlocks

Electrochemical Society Proceedings Volume 2003-26

were added for personnel and equipment protection. Heating jackets were added to all the vacuum isolation and throttle control valves.

In addition, the exhaust line was modified to add a 1.5 inch diameter bypass line with a small throttle valve used for control of pressures in the 2-100 Torr range during chamber cleaning. The bypass vacuum line was continued to rejoin the process effluent line at the vacuum pump. The process vacuum pump package (Edwards iQ80/iQ1200) was used for both deposition processing and for the chamber cleans. Beyond the pump an automated valve was used to switch the effluent stream between an absorption column type abatement unit (CS Clean) used for the fluorine cleaning by-products and a different CDO type abatement system used for the deposition process effluents.

To avoid deposits in the exhaust line beyond the pump, it is necessary to heat the line beyond the pump. The line from the pump to beyond the abatement-switching valve should also be heated.





IN-SITU CHAMBER CLEANING PROCESS

The baseline chamber clean identified uses NF₃ flow of 2 slm, N₂ dilution flow of 0.5 slm. The clean is carried out at a chamber pressure of 50 Torr, at a process temperature of 565° C. The furnace is maintained near the nitride deposition temperature ($565-^{\circ}$ C) while introducing a NF₃/N₂ gas mixture. NF₃ thermally decomposes at these temperatures, generating fluorine atoms that react with the CVD nitride film residue. This process provides good BTBAS nitride etch rate while minimizing attack of the quartz process tube, wafer carrier, and associated chamber parts.

Electrochemical Society Proceedings Volume 2003-26







Figure 4. FTIR absorbance spectrum

PROCESS MONITORING

Gaseous effluent from the AVP8000 was sampled at exhaust of the process pump using extractive Fourier transform infrared (FTIR) spectroscopy and quadrupole mass spectrometry (QMS). An FTIR absorbance spectrum and 110 amu mass spectrum are shown in Figs 4 and 5,

respectively. By products of the furnace clean are identified as unreacted NF_3 , SiF_4 , CF_4 , NO, and NO_2 .



Figure 5. 110 amu mass spectrum during the clean

The concentration of these byproducts was monitored in real time during the furnace clean (Fig. 6). This furnace clean follows a cumulative 0.20 μ m BTBAS nitride deposition (50 nm deposition). The major byproduct is unreacted NF₃. The SiF₄ is due to BTBAS etching and CF₄ is present because of residual carbon in the BTBAS film. After about 20 minutes, there is a sharp increase in the NO concentration. NO is a byproduct of quartz etching and indicates that the BTBAS nitride film has cleared, exposing the underlying quartz. The appearance of NO is accompanied by a decrease in the concentration of CF₄, also indicating that the BTBAS nitride film has cleared. The CF₄ and NO concentration profiles provide a good end point monitor. The furnace is cleaned using a 25-minute etch step following a cumulative BTBAS nitride deposition of 0.20 μ m.

PROCESS QUALIFICATION

The baseline process was qualified by passive data collection (40 run PDC). After 4 deposition batch cycles processing 100 wafers per cycle, (50nm BTBAS nitride), the furnace was cleaned using NF_3 then the chamber walls were nitride re-coated. BTBAS nitride 100 wafer deposition runs continued.

No change in wafer uniformity or deposition rate was observed following the NF₃ clean (Fig. 7). The within wafer and wafer to wafer uniformity and average thickness for all runs following the clean were the same as the prior 100 wafer deposition cycle before the clean. Wafer uniformity was also unchanged from the baseline uniformity measured in runs done before implementing the NF₃ chamber cleaning.







Figure 7. Total thickness and within wafer uniformity control over the 40 run PDC.

DEFECT CONTROL

Goals of <125 particle adder defects per wafer for size >0.10 μ m and <50 adders of size >0.16 μ m were met during the 40 run PDC using the NF₃ chamber clean process for the BTBAS nitride system as shown in Figure 8. Later work has shown that the number of runs between cleans can be extended to at least 7 for a total of 350 nm of deposition between in-situ cleans while

maintaining the same level of particle control. When the clean overhead can be spread over a greater number of deposition cycles, the clean contribution to overall system throughput is reduced.



Figure 8. Defect levels as measured for size >0.10 and >0.16 µm were maintained low through the 40 run PDC.

CUSTOMER SITE FIELD EXPERIENCE

An NF₃ chamber clean process has been transferred successfully to manufacturing sites running the BTBAS nitride process for advanced gate stack sidewall spacers. The process has been robust in a manufacturing environment and greater than 200 runs (20,000 wafers) are processed between any chamber maintenance other than the regular NF₃ in-situ clean done at intervals of 4-7 runs or 200-350 nm of film deposition. The robustness of the process has been demonstrated by the ability to recover from particle events produced by introduction of wafers with peeling deposits and/or poorly cleaned filler wafers by simply doing the NF₃ clean cycle and a qualification run. Field experience indicates the lifetime of quartz parts will be equal or greater using the NF₃ in-situ clean compared to using conventional wet cleaning. Because the cycle time to clean is short, the availability of the equipment is greatly enhanced.

CONCLUSIONS

We have developed an improved in-situ thermal process for cleaning LPCVD furnace quartzware following BTBAS nitride deposition. The NF₃-based process was optimized with respect to clean time, selectivity, and uniformity. FTIR and QMS were used to monitor the furnace clean and identify etch byproducts. The furnace is cleaned in 20 minutes following a

212

cumulative 0.20 µm BTBAS nitride deposition. The BTBAS nitride deposition process has been qualified following the clean (deposition rate, uniformity, particles) and the *in-situ* NF3 clean has been implemented to production manufacturing sites.

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Electrochemical Society Proceedings Volume 2003-26

MAKING SUPERCRITICAL CO₂ CLEANING WORK: PROPER SELECTION OF CO-SOLVENTS AND OTHER ISSUES

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Supercritical CO₂ (scCO₂) cleaning is an exciting green technology to remove heavy organics (resist and/or residue) with complete rinsing and drying of the wafer in one single step. However, there are a number of concerns about implementing scCO₂ cleaning in the industry. In this paper, those concerns are listed and some of them are addressed in detail. One of the challenges is selection of the proper co-solvent for scCO₂ processing. This paper will focus on the differences from ambient pressure cleaning, guidelines for choosing the correct co-solvent(s) for scCO₂ cleaning, the safety aspects of the scCO₂ tool and material compatibility issues. Consequences of selection of a suitable co-solvent mixture resulting in decreased process time, decreased chemical consumption and lower operating pressures are presented. The pros and the cons of both industry approaches to scCO₂ cleaning (using a mixture of co-solvents and/or using scCO₂ philic surfactants) are also discussed in detail.

INTRODUCTION

Supercritical CO₂ (scCO₂) cleaning has emerged as a viable technology to remove heavy organics (resist and/or residue) in one single step with complete rinsing and drying of the wafer.^{1,2} The first part of the scCO₂ cleaning step is removal of heavy organics from the wafer surface. The second part of the same scCO₂ cleaning step involves rinsing and drying the wafer and the high pressure process chamber. Compared to the current industry practice of multiple steps of dry etching, followed by a wet clean, followed by rinsing and drying of the wafer requiring multiple tools and/or different tanks in the same tool, scCO₂ cleaning in a single process chamber offers considerable environmental, technical and throughput advantages that have been detailed elsewhere.^{1,2}

However, there are a number of concerns about implementing $scCO_2$ cleaning in the industry. In this paper, those concerns are listed and some are addressed in detail. The challenges facing the semiconductor industry are using a high pressure system that is pressurized and depressurized several tens of times an hour and yet is safe to operate and is pristinely clean of particles and metals. The other challenge is selection of the proper co-solvent for $scCO_2$ processing. This paper will focus on considerations for selecting

Electrochemical Society Proceedings Volume 2003-26

the appropriate co-solvent(s) for $scCO_2$ cleaning, the safety aspects of the $scCO_2$ tool and material compatibility issues.

What are co-solvents?

Following one of the earliest chemical rules, "similia similibus solvuntur" (like dissolves like), the non-polar CO_2 by itself cannot dissolve the polar heavy organics. To attack the heavy organics, small amounts of polar chemicals (co-solvents) are added along with the scCO₂. The polar co-solvents are usually a mixture of solvents with some water, and are tailored to selectively remove only heavy organics only without affecting other materials in the stack. In this paper, an attempt is made to discuss the principles of selecting the proper co-solvent mixture (co-solvent 1) from first principles. Consequences of selection of a suitable co-solvent mixture, the pros and the cons of both industry approaches to $scCO_2$ cleaning (using a mixture of co-solvents and the using $scCO_2$ philic surfactants) and the principles behind the selection of 2^{nd} co-solvent that can rinse and dry the wafer will be discussed. Impact of the selection of the 1st co-solvent to remove heavy organics on process time and chemical consumption is discussed.

Differences from ambient pressure cleaning

As described in a previous publication,³ the most challenging heavy organics to remove are those that are created in semiconductor processing steps such as ion implantation & ashing and etching. The heavy organics produced are highly cross-linked and have undergone some outgassing (composition change) and phase transformations at the high temperatures generated in the processing step. For example, using Ar ions to sputter away implanted polymer films (for XPS depth profiling analysis) revealed the top surface of what was the polymer had been converted into graphitic amorphous carbon.⁴ Challenging heavy organics have been created at high temperatures in a highly reactive medium and therefore require even higher energy to break the inter- and intra- molecular bonds. At ambient pressures, the current method of removal involves exposing the wafers to semi-aqueous solvent solutions at temperatures ranging from room to 80 °C. These solvents contain toxic amines, do not do a satisfactory job of cleaning without sidewall attack, are unable to completely remove the residues from the sidewall and bottom of high aspect ratio vias and often undergo compositional changes because of evaporation of water. All these ambient pressure cleaning limitations can be overcome by scCO₂ cleaning with the proper co-solvents as detailed below.

The temperature and pressure needed to make CO_2 supercritical are insufficient to make the co-solvents supercritical and they exist as a liquid. This is because the cosolvent is highly polar and is often a semi-aqueous solution whose supercritical conditions need not be achieved to obtain complete removal of heavy organics. Given that the scCO₂ and co-solvent liquid are immiscible and have a large density difference, phase separation occurs with the lighter scCO₂ on the top and the heavier co-solvent at the bottom in contact with the wafer surface. So while the cleaning solution is still liquid at both ambient pressure and under scCO₂ cleaning conditions, the cleaning solution under supercritical conditions has decreased surface tension and viscosity and is able to penetrate and exit high aspect ratio vias. The cleaning solution at ambient pressure is not able to overcome gravity and surface tension to exit the high aspect ratio vias. Also under supercritical conditions, several liquids (including water) remain as liquid at temperatures exceeding their boiling point and do not evaporate.

Electrochemical Society Proceedings Volume 2003-26

While increasing process temperature is often used to speed up removal of heavy organics at ambient pressure, it is not desirable to increase the operating temperature and pressure as high as possible for $scCO_2$ cleaning. With increased pressure, the density of the $scCO_2$ also increases. As solvating abilities are directly proportional to density, beyond a certain range of pressures the $scCO_2$ will have stripping abilities without any co-solvent assistance. That is not desirable because the $scCO_2$ will not be stripping the heavy organics selectively; it will try to dissolve all the structures present on the wafer surface. Therefore, it is important to have an optimum pressure range (for selective removal of heavy organics) and temperature (for the wafer's thermal budget).

Selection of co-solvent 1

The ideal co-solvent 1 should be able to aggressively dissolve the heavy organic into itself, be completely miscible in the $scCO_2$, have a low vapor pressure, non-flammable, be environmentally friendly and stable in composition.

The low vapor pressure requirement makes the solvent have a high boiling point, low evaporation rate (stable in composition), a high flash point etc. Combining this requirement with the need for an environmentally friendly solvent considerably shortens the list of likely co-solvents. The ability to dissolve a highly cross-linked polymer means that the co-solvent needs to be highly polar, i.e., have a high dipole moment and a high dielectric constant. A review of reference data⁵ reveals that this is indeed the case, the solvents with the highest dipole moment and dielectric constants are the ones commonly used in commercial stripper formulations. The requirement of co-solvent 1 being highly polar to dissolve the photoresist and being completely soluble in non-polar scCO₂ means it needs to have both polar and non-polar groups. Since the primary purpose of cosolvent 1 is to dissolve heavy organics, co-solvent 1 needs to have a large polar component, i.e., it needs to have a short chain non-polar group attached to a large polar moiety. Extensive testing done at SCP Global Technologies and other research groups has revealed that there is no single solvent that is the ideal co-solvent 1; rather mixtures of various solvents are used as co-solvent 1.^{1,2} While some research groups in the industry are using scCO₂ soluble surfactants as a major part of their co-solvent 1 formulations, other research groups, including SCP, do not use them. The pros and cons of both approaches will be discussed in a later section.

The solvency power of a solvent has been summarized by Hansen who attempted to quantify polymer solubility in solvents.⁶ Hansen used the concept of the Hildebrand solubility parameter⁷ and added hydrogen bonding effects to define the Hansen solubility parameters (HSP). HSP are based on the premise that the total energy of vaporization of a liquid consists of several individual parts. These arise from dispersion forces (atomic interactions), permanent dipole-permanent dipole forces referred to as polar forces and hydrogen bonding forces (electron exchange). They are represented by the equation:

$$\delta^2_{\rm T} = \delta^2_{\rm D} + \delta^2_{\rm P} + \delta^2_{\rm H} \tag{1}$$

where δ_T is the Hansen solubility parameter, δ_D is the dispersive parameter, δ_P is the polar parameter and δ_H is the hydrogen bonding parameter. A polymer having similar HSP as a solvent or a mixture of solvents is soluble in the solvent (or solvent mixture). This is graphically represented in Figure 1.⁸ Figure 1 shows the projection of a HSP sphere for a given material with the radius of the solubility sphere, R, given by:

$$R^{2} = (\delta_{D,M} - \delta_{D,S})^{2} + (\delta_{P,M} - \delta_{P,S})^{2} + (\delta_{H,M} - \delta_{H,S})^{2}$$
(2)

Where the subscripts M refers to the material and S to the solvent. Solvent(s) that will dissolve the material will have HSPs that lie inside the sphere. Solvents with HSPs that lie outside this sphere will fail to dissolve the material. While there are other forces such as induced dipoles, metallic bonds, electrostatic interactions etc. that are not taken into account, the Hansen solubility parameters have worked remarkably well in predicting polymer solubilities in solvents. The use of HSPs in resist strippers is well known⁹⁻¹¹, and has been used to formulate co-solvents for scCO₂ cleaning applications.^{12,13}



Figure 1. Representation of a Hansen Solubility Parameter solubility sphere and its projections on 3 axial planes (from ref. 8).

2nd Co-Solvent

Given the difficulty of dissolving a polar solution such as co-solvent 1 into nonpolar scCO₂, a second co-solvent is needed to as a bridge solvent. The 2^{nd} co-solvent is soluble in co-solvent 1 and in scCO₂. Because of the need to act as a bridge solvent, the 2^{nd} co-solvent also has polar and non-polar groups. Once the heavy organic removal is complete, the 2^{nd} co-solvent is introduced into the pressurized chamber; its job is to dissolve the co-solvent 1 into itself and itself dissolve into the scCO₂. The introduction of the 2^{nd} co-solvent rinses co-solvent 1 off the wafer surface. Once enough 2^{nd} cosolvent is introduced to complete the wafer rinsing, depressurization of the chamber creates a differential pressure gradient that drives all the scCO₂ out of the chamber. With the 2^{nd} co-solvent acting as a bridge solvent, no liquid is left on the wafer surface and the wafer comes out dry.

Co-Solvents Used for scCO₂ Cleaning

As explained earlier, co-solvent selection based on HSPs has been quite successful in finding solvents that can dissolve polymers. Unfortunately, during the implant and plasma steps highly cross-linked and in many cases new heavy organics are

created. It is not practical to determine the HSP of these heavy organics, specially when their composition and hence their HSPs can be easily changed by small changes in the process step. It is also important to remember that HSPs are only *predictors* of dissolution and not a *measure* of dissolution. For these reasons, various research groups use the HSP number as a broad guideline to select solvents and rely on their experiences at ambient pressure removal of heavy organics to formulate co-solvent 1 mixtures for $scCO_2$ cleaning.

The ideal $scCO_2$ cleaning co-solvent formulation should dissolve both organic and inorganic residues. Therefore it should contain both organic and inorganic solvents along with 20-30% water to decrease flammability of the formulation. Since almost all the heavy organics the $scCO_2$ cleaning co-solvent is expected to remove will be heavily cross-linked, a strong oxidizer or reducing agent is needed to break the cross-linked bonds. This is because the strongest organic solvents only swell the cross-linked polymer modestly, certainly not enough to generate the stresses necessary to drive the crack propagation necessary to cause debonding. Oxidizers or reducing agents can be selecting from studying the oxidation potential table (ref. 5) while chelators and corrosion inhibitors are chosen depending upon the specific heavy organic to be removed.

Several research groups have used tried to use $scCO_2$ philic surfactants for cleaning. At first glance, use of these surfactants appears to be attractive as it avoids the need for a 2nd co-solvent to dissolve co-solvent 1 into $scCO_2$. Johnston et al. are using $scCO_2$ philic surfactants for cleaning and as a 2nd co-solvent that is soluble in $scCO_2$.¹⁴ Wagner and co-workers are using $scCO_2$ philic surfactants to form reverse micelles in $scCO_2$ in which acids, bases, etchants and other active chemistries are caged in order to accomplish $scCO_2$ cleaning.¹⁵ However, a closer examination reveals a number of reasons why these approaches may not be practical.

Firstly, the number of $scCO_2$ philic surfactants is very small and limited to silica based, fluorine based and some hydrocarbon based surfactants. All of the surfactants currently being tested are formulated in-house and tested in small quantities. Therefore, scaling lab procedures to industrial production of semiconductor purity grade $scCO_2$ philic surfactants makes these chemicals very expensive. In addition, the results of Johnston et al. show that none of the surfactants tested, by themselves, so far have been able to completely remove the heavy organics.¹⁴ This cleaning limitation has led Wagner et al. to use acids, bases, etchants and other active chemistries to aid surfactants in accomplishing cleaning.¹⁵ If the surfactant by itself cannot accomplish cleaning and is prohibitively expensive, it may not be a suitable cleaning choice.

There are also concerns about surfactants depositing on the PFA tubing used on the ambient pressure side of the hardware. Additional steps will be needed to verify that the surfactant is completely removed from the wafer surface. Apart from the recovery costs of the CO_2 insoluble active chemicals, additional costs will be incurred in recovering the expensive scCO₂ philic surfactants from the CO_2 once the scCO₂ is depressurized. Based on the needless complexity introduced for little technical advantage and additional cost of ownership, scCO₂ philic surfactants do not appear to be a good choice to accomplish scCO₂ cleaning.

218

The solvents used by most of the researchers for scCO₂ cleaning are based on solvents that are presently used for ambient pressure cleaning. These strippers contain toxic solvents and solvent combinations. Given the fact that most photoresists are acidic, the industry has tried to remove them using alkaline chemicals, most of them being amines. Amines tend to undercut the photoresist and the stripper solution is recirculated while the undercut photoresist is slowly dissolved in the amine solution or is trapped in a Using amines in scCO₂ cleaning has led to the conjoint action of scCO₂ filter. penetration of the heavy organic and swelling of the heavy organic with the scCO₂ and amine co-solvent. Undercutting of the heavy organic by the amine leads to the heavy organic being debonded and delaminated from the wafer surface. Several pressurization (ambient to operating pressure) and depressurization cycles along with recirculation of the co-solvent 1 mixture in a loop have been reported to clean 1 wafer (Figure 2).^{16,17} Repeated venting and filling of the process chamber multiple times wastes chemical inputs (scCO₂ and 2^{nd} co-solvent), increases wafer processing time and unnecessarily pressure cycles the process chamber.





While the amine solvents and solvents combinations were once accepted as useful, they have come under increasing public scrutiny and governmental regulation for the health and environmental risks they pose. It is possible to formulate strippers, from first principles outlined in this paper, that exhibit little or no human or environmental toxicity, are biodegradable & non-flammable and evidence little or no tendency to evaporate.¹⁸ Results in reference 18 show that choosing the proper mix of chemicals to make the co-solvent 1 formulation not only gives all the above listed desirable solvent traits, this formulation dissolves the photoresist and etch residues layer-by-layer. Therefore, it is possible to achieve "dry in, dry out" at a single operating pressure without any pressure cycling. Operating at a single pressure throughout the whole $scCO_2$ cleaning process results in decreased process time and chemical consumption and avoids the additional hardware needed to move the heavy organic, undercut by the amine cosolvent, off the wafer surface. Similar attempts to use megasonics in a high pressure, high temperature system to provide mechanical agitation to move the undercut heavy organic off the wafer surface¹⁹ are unwarranted. Additional pressurized reservoirs of scCO₂, in addition to the process chamber, to facilitate the numerous cycles of pressuring

Electrochemical Society Proceedings Volume 2003-26

and de-pressurizing the process chamber to mechanically remove the undissolved, undercut heavy organic are also not needed.²⁰ This is all made possible by using co-solvents that actually dissolve the heavy organic.¹⁸

Table 1 shows SCP results, from Figure 2, with highly implanted photoresist at 2400 psi and 100 °C and compares the results to those obtained by other researchers.²¹ Compared to a low dose implant, a heavy dose of implanted As is removed in 40% of the time at about half the operating pressure.

Challenge Wafer	Stripping Time (min:s)
As implant @ 20 keV, 3×10^{15} atoms/cm ² dosage (this work)	2:00
As implant @ 20 keV, 8 x 10 ¹⁵ atoms/cm ² dosage (this work)	4:00
"low" dose implant into DUV photoresist @ 4400 psi (ref. 21)	10:00

Table 1: Dosage of Implanted Photoresist and Stripping Time

Safety Issues for scCO₂ Cleaning

Supercritical fluid cleaning, extraction and synthesis equipment has been in production in many industries (food, pharmaceutical, perfume, waste destruction etc.). A lot of the proven technology can be quickly modified and adapted for use in the semiconductor industry. A complete tool, except the process chamber, can easily be built with wafer handling and CO_2 delivery and recycling capabilities. IC production requirements dictate that the tool be pressurized and de-pressurized several tens of times an hour for 24/7/365 operation. This requires that the process chamber have infinite cycle fatigue lifetime, high safety factors and that highly corrosion resistant materials be used for hardware construction. The exact choice of the corrosion resistant materials is dictated by the co-solvent mixture used. In case amines are used as co-solvents, the reaction between the acidic CO_2 and alkaline amines as well as amine stress corrosion cracking have to be accounted for.

SUMMARY

Supercritical CO_2 cleaning is a green and viable technology for IC manufacturing. One of the major concerns about its implementation in IC manufacturing is the proper choice of co-solvents. The proper selection of co-solvents that actually dissolve the photoresist, rather than undercut it, has been shown to lead in substantial reduction in process time, chemical consumption and lower operating pressures. This also avoids the use of additional high pressure scCO₂ reservoirs, pumps, filters and other equipment to recirculate the undercut heavy organic and fragile equipment like megasonics in a high temperature, high pressure system.

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CHEMICAL ADDITIVE FORMULATIONS FOR SILICON SURFACE CLEANING IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

We have investigated the removal of ion-implant photoresist, postetch process residues and particles for various patterned semiconductor wafers using supercritical carbon dioxide (SCCO2)/chemical additive formulations. Optimization of the chemical formulations was determined using data obtained from statistical analysis and designed experiments. Characterization of the processed samples via scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy, Fourier transform infrared spectroscopy (FTIR) and ellipsometry revealed that process conditions and chemical derivatization are important to cleaning patterned wafers. The results of our investigations illustrate the potential of SCCO2 as a viable cleaning technology for next-generation integrated circuits, as well as micro electro machining systems (MEMS).

INTRODUCTION

As semiconductor device architectures continue to shrink, small-feature/highaspect ratio trench and via structures have become common in the devices. These structures are formed in close proximity to each other and can become physically bonded together due to the high surface tension of water during the wetting and subsequent drying of the structures in an aqueous cleaning. This phenomenon, called stiction, is a common problem in the manufacturing of micro electro mechanical systems (MEMS) devices [1]. Therefore, removal of contamination on these structures without pattern collapse or stiction is difficult.

Historically, photoresists and residues are removed from silicon surfaces in a Piranha bath in FEOL processing or by a combination of dry ashing and wet clean steps in BEOL processing [2]. As these processes are costly, use large amounts of hot, aggressive and toxic chemicals, can have large water usage and disposal costs, the semiconductor industry is searching for alternate cleaning processes that accomplish the same cleaning while using smaller quantities of chemicals.

222

Supercritical carbon dioxide (SCCO2) provides an alternative method for cleaning. SCCO2 diffuses rapidly, has low viscosity, near zero surface tension like a gas, and thus, can penetrate easily into deep trenches and vias. It also enables more effective cleaning without pattern collapse or stiction. SCCO2 has the solvating properties of a liquid and thus can dissolve chemicals, such as alcohols and amines, forming a homogenous supercritical fluid solution. SCCO2 is non-polar and has the ability to solvate non-polar chemicals. However, it will not solvate many species, including inorganic salts and polar organic compounds that are usually necessary for efficient cleaning. Therefore, cosolvents and/or chemical additives are used in conjunction with the SCCO2 fluid to increase the solubility or enhance the dissolution of these species.

In this paper, we have successfully demonstrated removal of particles, removal of post-etch residues, and removal of high-dose ion-implant photoresists by the appropriate choice of chemical additives in supercritical CO_2 formulations.

EXPERIMENTAL METHODS

Figure 1 shows a schematic diagram of the high-pressure system designed to study the feasibility of supercritical CO_2 cleaning of semiconductor surfaces. The system is composed mainly of: (1) two high-pressure 316 stainless steel vessels, one serving as a dynamic mixer/mass exchanger (MIX) while the second is the wafer cleaning chamber (WCC). (2) A high-pressure gas booster (GB) to maintain a constant flow and/or pressure of the supercritical fluid, and (3) an HPLC sample pump (SP) to deliver the co-solvent/chemical modifier solutions to the mass exchanger.



Figure 1. Schematic diagram of the continuous flow SCCO2 cleaning apparatus used in these studies.

223

In a typical cleaning experiment, a sample wafer $(20 \times 20 \text{ mm})$ was loaded into a 1.5 in. ID stainless steel wafer cleaning chamber with adjustable volume (25 - 100 mL). High purity carbon dioxide (99.999%; Tech Air) from a gas cylinder is fed through a gas booster and subsequently chilled through a cooling cylinder (CC) to insure that the CO₂ is under cooled and can be easily compressed by the high-pressure CO₂ pump (CP) before introduction into the CO₂ heater.

The heated CO_2 and co-solvent are then delivered to the mixing chamber (MIX) via separate delivery lines and can be mixed either in a dynamic or static mode before being transferred to the wafer-cleaning chamber (WCC). In the cleaning chamber, the pressure is adjusted by a backpressure regulator (BPR) to the desired level and controlled to within 0.14 MPa. The CO_2 heater, mixer and cleaning chamber are heated using electrical resistance tapes, that are controlled by a multi-loop temperature controller and provide a stable temperature to within ± 1 °C. In addition, each pressurized vessel is equipped with a pressure transducer to monitor the pressure inside the vessel. After cleaning was complete, the SCCO2/chemical solution was purged from each individual chamber separately, as to not contaminate the processed wafer from chemical remaining in the mass exchanger, and vented into a high pressure trap to collect any residual chemicals and/or wafer residue during the phase separation induced by the venting process.

RESULTS AND DISCUSSIONS

Particle Removal

224

It is well known that particle contamination and process residues can cause detrimental effects on the performance and yield of semiconductor devices [3]. Additionally, the cost of manufacturing a semiconductor wafer is proportional to the time employed for each processing step. Thus, it would be advantageous to remove particle contamination and post-etch residues without using expensive process equipment and with a minimum of process steps.

The high solvating power of supercritical carbon dioxide makes this method a viable alternative for fast and safe wafer cleaning. High turbulence at the wafer surface features, in conjunction with hyper-efficient mass transport of a chemical co-solvent mixture, can clean the wafer surface in very short processing times. The particles are effectively removed without direct mechanical contact, in contrast to current methods and the wafer surface contains fewer defects as compared to mechanical scrubber methods. The density at pressures significantly above the critical point of carbon dioxide is nearly equal to that of a liquid state; thus, supercritical carbon dioxide carries the co-solvent/chemical additive mixtures onto the wafer surface and removes the particle contamination on the semiconductor device.

The effectiveness of SCCO2 for the removal of surface particles, specifically SiO_2 patterned silicon wafers contaminated with non-spherical Si_3N_4 particles (0.2 - 2.0 μ m), was investigated. Novel cleaning formulations were explored using several different chemical additives and surfactants, and combinations thereof. The wafers were processed

in a SCCO2/chemical additive solution (the term chemical additives includes a mixture of co-solvent and specific chemical components and will be referred to as such throughout this paper) at the optimized conditions of 50 °C and 31 MPa. The multi-component cleaning solution, consisting of a fluorinated surfactant, an etchant and surface passivation additives, resulted in nearly 100 % removal of the Si₃N₄ particles on both the silicon and silicon dioxide layers with little etching of the underlying layers.

Figure 2a shows an SEM image of the Si_3N_4 contaminated control wafer depicting the wide size distribution and irregular shape of the particles. The black and grey areas in the SEM photo represent the silicon and silicon dioxide surfaces, respectively, and the white spots are the Si_3N_4 particles. Due to the differing surface characteristics of the materials, i.e. hydrophobic silicon layer and hydrophilic dioxide layer, a three-component chemical additive system was determined necessary for the complete particle removal without damaging the underlying layers (Figure 2b). The three-component cleaning solution consisted of an etchant and surface passivation additives for both the silicon and silicon dioxide layers. Each additive (surfactant) indirectly aided in particle removal by competing with the van der Waals forces responsible for the adhesion of these particles to the surfaces. Thickness measurements were taken before and after processing, and silicon and silicon dioxide etch rates as low as 2 Å/min were obtained.



Figure 2. SEM images of (a) control wafer displaying the random distribution of the Si_3N_4 particles and (b) wafer processed using a SCCO₂ cleaning solution containing a fluorinated surfactant, a non-fluorinated surfactant and an etchant.

Aluminum Post-Etch Residue Removal

Photolithography is widely used for defining patterns in multi-layered thin films. After aqueous development of the image, reactive ion etching (RIE) is used to transfer the pattern to under-lying layers. The etching process usually results in the formation of a tough, cross-linked crust that protects the underlying bulk photoresist. Conventional methods of cleaning often employ an oxygen-plasma ash, often in combination with halogen gases, to penetrate the crust and remove the photoresist. Unfortunately, plasma

225

ashing oxidizes the metal interconnect and organic dielectric layers, leaving an inorganic residue that may contain stable oxides and halides of the underlying layer constituents. Currently, removal employs wet processes that result in aqueous waste streams. We have demonstrated, however, that SCCO2 cleaning has the capability to remove the post-etch residue in a single step, while incorporating short process times and consuming only small amounts of chemical additives.

Screening of various chemical additives was first performed to determine potential cleaning additives for post-etch residue removal of aluminum films etched by reactive ion etching. Results showed that a multi-component system consisting of an organic co-solvent, an etchant, a hydroxyl-containing chelator for etch residue removal and a corrosion inhibitor for aluminum and poly-silicon was successful for complete residue removal. The dissolution mechanism of the residue can involve fluorination or chelation of the metal residue as depicted in the following schemes:

Scheme 1: Fluorination



In Scheme 1, the metal ion is converted to an oxyfluoride, while in Scheme 2, the metal ion is chelated by an organic group. In both cases, the products are significantly more soluble in the SCCO2/co-solvent solution than the original residue.

The chelating ligands must be appropriately matched with the metal of residue. For instance, aluminum (III) is a hard acid and, as such, prefers hard bases such as fluorine or oxygen. Aluminum cations bind firmly with negatively charged organic functional groups. This can best be seen by the high stability of the $Al(OH)_4^-$ complex in the very high pH regime, where the log stability constant *K*, is 8.31 for $Al(OH)_4^-$, where *K* is the value for the reaction of Al^{3+} with the completely deprotonated ligand, OH⁻. In theory, the higher the *K* value, the higher the stability of the aluminum complex. Moreover, because of the chelating effect, complexes of higher stabilities are demonstrated by bidentate and multidentate ligands, with the donor groups typically

being hydroxyl, carboxylate or amine groups, such as those used in our experiments. These ligands all exhibit K values in the range of 12-16, which are much higher in comparison to the very stable Al(OH)₄⁻ complex mentioned above, suggesting that these chelating ligands are very efficient for the removal of aluminum cation residues.

This SCCO2/chemical additive formulation and process was then optimized using design of experiment and the optimum conditions were determined to be 35 °C and 28 MPa. Figure 3a shows the SEM image of the sample with post-etch residues before cleaning while Figure 3b shows the same wafer after SCCO2 cleaning. It is clear from the SEM images that the white, translucent strip of residue along the trench edge and sidewall is completely removed with minimal impact on critical dimensions of metal lines and trenches, and without corrosion and grain-size change of the Al films, after 120 seconds exposure to the SCCO2 cleaning formulation. It should be noted that the active chemical concentrations represent values less than 1 wt % total in the SCCO2 solution. Electrical measurements taken before and after SCCO2 processing reveal aluminum etch rates of less than 1 Å/min.

Pattern degradation of the fragile air-bridge structures of MEMS devices was prevented using the same SCCO2 chemical formulation employed for the aluminum postetch residue removal process.



Figure 3. SEM images of the samples with post-etch residues (a) before cleaning and (b) after SCCO2 cleaning; and (c) a MEMs test structure processed using conventional wetcleaning methods; (d) a MEMs test structure processed using the same SCCO2 formulation employed for the aluminum post-etch residue removal process in (b).

Figure 3c shows a sample wafer consisting of a MEMS structure with an airbridge length, $100 \mu m$, which was soaked in deionized water followed by air-drying. The high surface tension of water causes collapsing of the bridges, commonly referred to as stiction, and the stiction is clearly observed (by SEM) in Figure 3c. It should be noted that similar results were observed using organic solvents that also possess relatively low surface tension. Figure 3d depicts a MEMs test structure processed using the same processing conditions and SCCO2 formulation employed for the aluminum post-etch residue removal process and reveals no structural damage of the air-bridges. Once the cleaning process was complete, the cleaning chamber was rapidly depressurized to atmospheric pressure in less than 60 seconds. We have found that both rapid and slow de-pressurization modes lead to non-stiction, suggesting that the most critical step in the process is to completely remove any residual water and co-solvent after cleaning and before de-pressurization, in order to eliminate stiction. After the process is complete, as long as the wafer is in a dry environment, the mode of de-pressurization is of little significance.

Photoresist Removal

The complete removal of polymeric photoresist, exposed either to deep UV light and/or to high-dose ion implant, is problematic for conventional stripping and cleaning methods. Ion implantation treatment results in the formation of a tough, carbonized crust that renders removal of the underlying bulk photoresist difficult. Due to the low viscosity of SCCO2 cleaning solutions, they can effectively penetrate, swell, and subsequently remove the photoresist without damaging the underlying structure. Some have reported that employing a SCCO2 process that involves pressurization/depressurization to debond the resist from the substrate and carry it away using flow dynamics [4]. However, this leads to increased processing times, cost, and chamber fatigue, not to mention potential clogging of lines due to the delaminted photoresist. Therefore, we have chosen to take a dissolution route for removal of photoresist using a constant pressure and active chemistry.

We have found that the addition of polar alcohol co-solvents, to SCCO2 is effective for removal of low-dose (As: 2×10^{13} /cm²) ion-implant photoresist at 35 °C and 28 MPa for 120 seconds. However, co-solvents alone proved to be ineffective for removing medium (As:2 \times 10¹⁴/cm²) and high-dose(As:2 \times 10¹⁵/cm²) implant hardened photoresist. We have demonstrated, however, that the addition of small amounts (< 1 wt%) of chemical additives aids in the removal of the high-dose ion-implant photoresist from a silicon surface. Several chemical approaches were investigated including solvation with organic solvents, oxidation, reduction, and fluorination, the latter two forming volatile, or very SCCO2-soluble fluorides or hydrides, thus leading to more favorable removal processes. The former two approaches yielded partial delamination of the photoresist, while the latter two, fluorination and reduction of the photoresist, completely removed the implanted photoresist via a dissolution process. Figure 4a shows an SEM image of a high-dose ion-implant (As: 2×10^{15} /cm²) photoresist control wafer consisting of the following stack: Si/SiO₂ (8 nm)/implant photoresist (~700 nm)/hardened crust (~40 nm). After processing the wafer for 30 seconds in an SCCO2/co-solvent

formulation at 55 °C and 28 MPa, SEM analysis showed that the photoresist was mostly being dissolved laterally from the edges of the resist, and only from the top-down in certain areas of the blanket layer. This is expected due to the 40 nm hardened crust on top of the photoresist due to the implantation process. Although the crust is somewhat permeable in the high diffusivity SCCO2 solution, dissolution is faster at the edges of the photoresist since no crust is present in these areas. Figure 4b shows the wafer completely stripped of photoresist while leaving the surrounding SiO₂ layer and underlying silicon substrate untouched by the SCCO2/co-solvent formulation.



Figure 4. SEM image of the (a) ion-implanted DUV photoresist control sample and (b) completely stripped sample wafer after processing for 120 seconds minutes at 55 °C and 28 MPa using a SCCO2/chemical additive formulation including a co-solvent.

Figure 5 shows an FTIR spectrum of a high-dose implanted resist control sample and the same sample processed using a SCCO2/chemical additive formulation at 50 °C and 28 MPa for 2 minutes. The control sample is characterized by a broad peak centered at ~3400 cm⁻¹, corresponding to hydroxyl (OH) group stretches [5]. The photoresist control sample is also characterized by a methyl (CH₃) group at 2979 cm⁻¹ and methylene $v_{as}CH_2$ (asymmetric stretch) and v_sCH_2 (symmetric stretch) groups located at 2923 cm⁻¹ and 2847 cm⁻¹, respectively. The small peak at 3019 cm⁻¹ is the signature peak for aromatic ring C-H stretching. Peaks located at 1733 cm⁻¹ and 1758 cm⁻¹ correspond to carbon-oxygen stretching of the double bond (C=O). Peaks located at 1613 cm⁻¹, 1505 cm⁻¹ and 1449 cm⁻¹ result from carbon-carbon stretching within the ring. The underlying silicon surface is represented by the silicon bonding vibrations in the 700-1400 cm⁻¹ region. The lower FTIR spectrum in Figure 5 illustrates the disappearance of these characteristic bands associated with organic polymers (i.e. -CH, -OH, C=O, etc.), indicating that the photoresist is completely removed under these process conditions.

Electrochemical Society Proceedings Volume 2003-26



Figure 5. FTIR spectrum of (a) post-SCCO2 processed sample after processing for 2 minutes at 50°C and (b) the pre-SCCO2 processed sample.

CONCLUSIONS

Through designed experiments, we identified SCCO2/chemical additive cleaning chemistries for high-dose ion-implant photoresist stripping, aluminum post-etch residue and Si₃N₄ particle removal, while maintaining the structural integrity of the wafer structure. In some cases, small amounts (< 0.1 wt%) of aluminum and silicon surface passivators were added to the SCCO2/chemical additive formulations to reduce surface attack. Data generated from the regression analysis showed that both individual chemical additive concentrations and relative ratio of the additives are important for optimal cleaning, as well as the process time and pressure. Moreover, the experimental process window for all of these cleaning solutions is quite large, making scalability less cumbersome.

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Electrochemical Society Proceedings Volume 2003-26

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SURFACTANT ENABLED CO₂ CLEANING PROCESSES FOR BEOL APPLICATIONS: POST BARRIER BREAKTHROUGH

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ABSTRACT: Low k films required to enable smaller feature sizes on IC chips call for development of new post breakthrough (BT) cleans that are effective and more compatible with the relatively fragile nature of these materials. Water-in- CO_2 microemulsions combine the process advantages of supercritical CO_2 with the solvent strength required to remove highly polar post BT cleans. This paper describes the use of water-in- CO_2 microemulsions as the basis for effective post BT cleaning formulations on patterned JSR 5109, dense SiLKTM and porous SiLKTM wafers. Favorable results from compatibility studies with these clean formulations on blanket low k films using spectroscopic ellipsometry, FTIR spectroscopy and Al dot tests will also be described.

BACKGROUND

The semiconductor industry continues to produce faster integrated circuit (IC) chips with smaller feature sizes. The introduction of Cu metallization and dielelctric films with k<3 (low k) has enabled chip production at the 90 nm node, but not without substantial integration issues, particularly related to ineffective cleaning and low k damage during wafer processing. Our group (1,2) and others (3,4) have examined scCO₂ based processes in back-end-of-line (BEOL) semiconductor wafer cleaning. It is expected that scCO₂ based cleans may have potential advantages over existing aqueous cleans in several areas. An all dry scCO₂ based process should have better compatibility with low k films and is unlikely to form hydrophilic groups on the dielectric that produce higher effective k values. Indeed, it has been demonstrated by several groups (5,6) that scCO₂ can be used to remove water and repair existing damage on low k. The absence of surface tension in scCO₂ will also provide enhanced wetting and facilitate penetration and rinsing of small feature sizes in the hydrophobic low k material. This is especially important for porous low k films.

Recently, we have focused on developing cleans for post etch, post ash, post breakthrough (BT) wafers with exposed Cu lines. The residue composition on post BT wafers is somewhat dependent on the specific low k material and etch/ash chemistry, but consists largely of oxidized Cu species. Effective cleaning of these wafers requires solvation and removal of oxidized Cu complexes as highly polar ionic species. The critical step in this pathway is a charge dissociation step, illustrated in Equation 1, where CuX₂ represents a generic form of an oxidized copper complex found in post BT residue.

$$CuX_2 \longrightarrow Cu^{+2} + 2X^-$$
 [1]

Charge dissociation of oxidized metal complexes creates multiple ionic species in solution, and can only take place in highly polar, protic media such as water that can solubilize the polar ionic groups.

Electrochemical Society Proceedings Volume 2003-26

A significant challenge in using scCO₂ for post BT cleans is that it is extremely non-polar, and will absolutely not support the charge dissociation and solvation of highly polar ionic species necessary for effective cleaning. Addition of polar cosolvents to $scCO_2$ in small quantities (<20%) will give a homogenous solution of slightly increased polarity, but one that will still not support ionic dissociation and solvation. It may be possible to add polar cosolvents to $scCO_2$ at levels above 20% to give a uniform solution of sufficient polarity to support ionic species, but at the cosolvent levels that would be required, the process advantages of scCO₂ are lost. Successful post BT cleans in scCO₂ requires chemistry that can be added in small amounts to CO₂ to create a heterogenous system of discrete polar microdomains dispersed in a continuous phase of non-polar CO₂. This is best achieved through water-in-CO₂ microemulsions.

Water-in-CO₂ microemulsions were first explored in the early 1990's (7,8) and offer a way to provide the process and environmental advantages of scCO₂ with improved solvent strength for polar molecules. Analogous to the structure of detergents that contain hydrophilic and oleophilic portions, surfactants for water-in-CO₂ microemulsions contain one segment that is CO₂-philic (favorable interactions with CO₂) and one segment that is hydrophilic. Most of the work described in this paper has been done with ionic surfactants containing non-alkali counterions. For post BT cleans, the polar domains in a water-in-CO₂ microemulsion serve two very important functions. First, they provide a medium for solvation and removal of the water soluble polar species that already exists in the post BT residue. Based on experimental results that we have achieved using just water-in-CO₂ microemulsions, this capacity enables removal of 80+% of post BT residue. The second function of the polar domains is to deliver active chemistry that can be used to modify the post BT residue to increase its water solubility and provide faster and/or better clean results. Typical aqueous based commercial cleans contain one or more types of active chemistry, such as acids, bases, chelants, etchants, oxidants, etc. We have used water-in-CO2 microemulsion systems that contain one or more of these active chemistries and found them to be highly effective at removing post BT residue rapidly and completely.

This paper will describe post BT clean and compatibility test results for patterned wafers containing JSR 5109, dense SiLK[™] and porous SiLK[™] as the dielectric film.

POST BREAKTHROUGH CLEAN RESULTS

JSR 5109 Wafers

A post BT wafer containing JSR 5109 as the low k material was obtained with the structure shown below in Figure 1.



Figure 1. Structure of post BT JSR 5109 wafer

Electrochemical Society Proceedings Volume 2003-26

The majority of clean formulation development for this wafer was done on wafer fragments in a 10 cc view cell. Initial screening of microemulsion and nonmicroemulsion based formulations verified that water-in-CO₂ microemulsions were the most effective at removing post BT residue. Microemulsions containing only surfactant and water in CO₂ produce a wafer that is roughly 80% clean (see Figure 3a). Incorporation of additional active chemistries to the microemulsion is required to produce wafers that are 100% clean.

Figure 2 shows SEM and TEM images of the post BT 5109 wafer, as received and after processing with a water-in-CO₂ microemulsion containing active chemistry, and a process-of-record (POR) aqueous clean. Figure 2a is an SEM image of the as-received wafer sample, showing granular residue on the floor and lower wall of the via, along with a white residue band halfway up the via wall. Figure 2b shows that virtually all the residue has been removed in the scCO₂ processed sample. Figure 2c is an SEM of the aqueous cleaned sample that shows all residue removed form the via floor but some of the white residue band remaining on the wall. A z-contrast TEM image of the as-received wafer in 2d clearly shows the buildup of Cu containing residue on the lower half of the via walls. Figure 2e shows the CO₂ processed wafer with all residue removed and no CD loss in the low k and no Cu overetch. Figure 2f is a TEM image of the aqueous cleaned sample that shows all residue removed from via floor but some remaining on the via sidewalls. Based on these images, it is clear that a water-in-CO₂ microemulsion formulation provides excellent cleaning results for post BT 5109 wafers that compare favorably with a POR aqueous cleane.



Figure 2. SEM and TEM images of post BT JSR 5109 wafer; (a) and (d) show the as-received wafer; (b) and (e) show the wafer processed with water-in-CO₂ microemulsion containing active chemistry; (c) and (f) show a POR aqueous cleaned sample

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Scale up of post BT JSR 5109 cleans from the view cell to a 200 mm prototype tool has begun. The first attempt on this wafer using a water-in-CO₂ microemulsion formulation with no active chemistry was very promising. Figure 3 shows a series of SEM images comparing the view cell processed wafer fragment to wafer samples processed in the 200 mm tool at center, middle and edge radius positions of the wafer. Similar cleaning results observed for all four wafer pieces in this series of images verifies that it is possible to scale up water-in-CO₂ microemulsions in a 200 mm prototype tool and get uniform, center to edge cleaning results that are comparable to those observed in the view cell. We are currently awaiting e-test results for post BT JSR 5109 wafers

processed in the 200 mm prototype tool with a water-in-CO₂ microemulsion containing active chemistry.



Figure 3. SEM images of post BT 5109 wafer processed with a water-in-CO₂ microemulsion containing no active chemistry; (a) is processed in a view cell; (b), (c) and (d) are processed in a 200 mm prototype tool at center, middle and edge radius positions, respectively.

Dense SiLKTM Wafers

A post BT wafer containing dense $SiLK^{TM}$ as the low k material was obtained with the structure shown below in Figure 4.





Initial screening experiments in the view cell again indicated that water-in-CO₂ microemulsions provided the best clean results. Figure 5 shows SEM images of an asreceived dense SiLKTM wafer and one that has been processed with a water-in-CO₂ microemulsion containing active chemistry. Note that these wafers did not contain any vias and so trench areas were examined by SEM to assess cleaning effectiveness. In these images, wafer fragments were fractured parallel to the trenchs to get the best look at post BT residue. The as-received sample shows a grainy residue on the trench bottom and slight residue on the lower wall. In the scCO₂ processed sample, all the floor residue has been removed and lower wall residue as well, as evidenced by the visible lower breakthrough layer.



Figure 5. SEM images of post BT dense SiLKTM wafer; (a) as received wafer; (b) processed with a water-in-CO₂ microemulsion containing active chemistry

Porous SiLKTM Wafers

A post BT wafer containing porous $SiLK^{TM}$ as the low k material was obtained with the structure shown below in Figure 6.

Electrochemical Society Proceedings Volume 2003-26



Figure 6. Structure of post BT porous SiLKTM wafer

Screening of various combinations of clean formulations once again indicated that water-in-CO₂ microemulsions provided the best cleaning results on post BT porous SiLKTM. Moreover, the same formulations that were most effective on dense SiLKTM cleans worked best for porous SiLKTM as well. Figure 7 shows SEM and TEM images of the as-received post BT porous SiLKTM wafer and one that has been processed with the same water-in-CO₂ microemulsion formulation used for the dense SiLKTM wafer imaged in Figure 5b.



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Figure 7. SEM and TEM images of post BT porous SILKTM wafers; (a) and (c) show the as-received wafer; (b) and (d) show the wafer after processing with water-in-CO₂ microemulsion containing active chemistry

As with the dense SiLKTM wafers, SEM images were taken from samples broken parallel to the trenchs. TEM images were taken from a FIB prep perpendicular to the trenchs. The as-received sample shows granular residue on the floor of the trench and some residue on the bottom of the trench wall by SEM, and clearly visible Cu containing floor residue by TEM. The scCO₂ processed sample shows complete removal of all residue by SEM and TEM. The floor of the trench is smooth and the bottom breakthrough layer in the wafer stack is clearly visible. No low k undercutting or Cu overetch is visible.

COMPATIBILITY RESULTS

Having demonstrated successful post BT residue removal from wafers containing several different types of dielectric films, we wanted to test the compatibility of the more effective clean formulations with the dielectric materials. This section will describe results from compatibility studies based on spectroscopic ellipsometry, FTIR spectroscopy and Al dot tests.

236

Spectroscopic Ellipsometry

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Spectroscopic ellipsometry was used to assess compatibility by measuring the film thickness and index of refraction (n) for blanket low k films on as-received and $scCO_2$ processed samples of JSR 5109, dense $SiLK^{TM}$ and porous $SiLK^{TM}$. All processed samples were run in a view cell with clean formulations based on water-in-CO₂ microemulsions containing active chemistry. The most effective clean formulations for each low k were tested for compatibility by exposing the blanket low k films to the cleaning process conditions then analyzing them by spectroscopic ellipsometry. A summary of the results is given in Table I. The JSR 5109 wafer shown in images 2b and 2e was processed with $scCO_2$ Clean B, $scCO_2$ Clean D was used to clean the dense $SiLK^{TM}$ wafer imaged in 5b, and the porous $SiLK^{TM}$ wafer shown in 7b and 7d.

Table 1. Spectroscopic Empsonetry Data for Blanket Low & Finns								
Low k film	Process ID	Thickness (A)	Δ Thickness (%)	n	∆ n (%)			
JSR 5109	scCO2 Clean B	3953	-0.18	1.2495	0.61			
	scCO2 Clean A	3925	0.53	1.2550	0.17			
	scCO2 Clean C	3961	-0.38	1.2525	0.37			
	As received*	3946 +/-10	n/a	1.2572 +/-0.005	n/a			
Dense SiLK	scCO2 Clean D	6141	0.07	1.6240	0.39			
	scCO2 Clean E	6160	-0.24	1.6243	0.37			
	scCO2 Clean B	6130	0.24	1.6255	0.29			
	As received*	6145 +/-10	n/a	1.6303 +/-0.005	n/a			
Porous SiLK	scCO2 Clean D	3139	0.32	1.4694	0.68			
	scCO2 Clean E	3147	0.06	1.4739	0.37			
	scCO2 Clean B	3147	0.06	1.4690	0.70			
	As received*	3149 +/-10	n/a	1.4794 +/-0.005	n/a			

ble I.	Spectrosco	pic Elli	psometry	Data	for	Blanket	Low I	k Films
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* As received data is based on average measurement of six different samples

As shown in the table, all tested formulations showed excellent compatibility with the blanket low k films. There was no change in film thickness or index of refraction that was greater than 1% and most of the data is within the noise of the measurement. Note also that there is overlap among the most effective cleans for all three low k wafers – i.e. Clean B was a very effective clean for patterned wafers containing JSR 5109, dense SiLKTM and porous SiLKTM. This supports the idea that the majority of post BT residue is oxidized Cu complexes, regardless of the low k material or previous process conditions, and that the key to effective cleaning is removal of these highly polar species. The generality of these cleans also implies that it may be possible to develop a single post BT cleans formulation that can be used with multiple low k films.

FTIR Spectroscopy

Following the spectroscopic ellipsometry measurements, the same set of samples was analyzed by FTIR spectroscopy to determine if there was any difference between the as-received films and those that had been scCO₂ processed. For each low k film, the same three clean formulations examined in the ellipsometry measurements were

Electrochemical Society Proceedings Volume 2003-26

compared to an FTIR spectrum of the as-received blanket film. Figure 8 shows overlay FTIR spectra for each low k film.



Figure 8. FTIR spectra of as-received and scCO₂ processed blanket low k films; (a) JSR 5109; (b) dense SiLKTM; (c) porous SiLKTM

FTIR spectroscopy supports results from the ellipsometry measurements. No change in the blanket low k film properties is observable after processing with effective $scCO_2$ clean formulations based on water-in-CO₂ microemulsions with active chemistry.

Al Dot Tests

238

Compatibility between the two SiLKTM blanket films and scCO₂ clean E was examined further through Al dot tests to measure the electrical properties of the processed blanket film. Two blanket wafers each of dense SiLKTM and porous SiLKTM low k films were exposed to scCO₂ clean E containing a water-in-CO₂ microemulsion with active chemistry in the 200 mm prototype tool. These wafers were then submitted for Al dot testing to determine k value, breakdown voltage and leakage current. A summary of the results is given in Table II. For both porous and dense SiLKTM films, the electrical properties of the wafers processed with scCO₂ clean E were all within an acceptable range of the unprocessed wafer.

Wafer ID	Process	ĸ	Vbd (MV/cm @ 1e-5 A/cm2)	standard deviation	Leakage Current (@ 0.5 MV/cm)	standard deviation	Leakage Current (@ 1.0 MV/cm)	standard deviation
Dense SiLK	CO2 clean E	2.65	5.27	0.03	1.19E-09	7.21E-11	2.49E-09	7.54E-11
Dense SiLK	CO2 clean E	2.64	4.89	0.39	1.29E-09	4.99E-11	2.86E-09	2.00E-10
Dense SiLK	as received	2.6	>4		<5 E-10		<5 E-10	
Porous SiLK	CO2 clean E	2.24	4.02	0.55	7.44E-10	4.37E-11	1.38E-09	2.43E-11
Porous SiLK	CO2 clean E	2.21	3.46	0.14	7.60E-10	2.67E-11	1.39E-09	1.36E-11
Porous SILK	as received	2.2	4 - 5		1 E-10		1 E-10	

Table II. Al Dot Test Results for Porous and Dense SiLKTM Blanket Films

CONCLUSIONS

This paper has described work done toward developing $scCO_2$ based processes for post BT cleans on low k wafers. Water-in-CO₂ microemulsions containing active chemistry were shown to produce excellent cleaning results on post BT patterned wafers containing JSR 5109, dense SiLKTM and porous SiLKTM as the dielectric material. Substantial overlap between effective cleans for the various low k wafers was observed. Comparison of as-received and scCO₂ cleaned wafers by spectroscopic ellipsometry, FTIR spectroscopy and Al dot tests indicated excellent compatibility between the waterin-CO₂ microemulsion cleans and the low k films.

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Electrochemical Society Proceedings Volume 2003-26

CO₂-EXPANDED LIQUIDS AS ALTERNATIVES TO CONVENTIONAL SOLVENTS FOR RESIST AND RESIDUE REMOVAL

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Gas-expanded liquids (GXLs) are a promising alternative to conventional solvents used extensively in microelectronics processing. GXLs have superior mass transport properties relative to liquids, but can maintain the solvent strength necessary for integrated circuit (IC) processing steps such as residue removal and photoresist stripping. Concurrently, the environmental benefits associated with CO₂-based processes can be substantial. Physical properties such as interfacial tension and viscosity, for example, can be decreased by over an order of magnitude in a GXL. The impact of this tunability on dielectric compatibility, feature collapse, and dissolution rate is discussed. CO2expanded ethanol largely maintains the solvent strength of pure ethanol for the dissolution of thin films of poly-hydroxystyrene (PHOST)-based photoresist. GXLs containing up to 75% CO₂ completely remove PHOST films from silicon substrates. Results of CO2-expansion of several solvents will be discussed as they relate to cleaning and surface preparation.

INTRODUCTION

Photoresist removal is one of the most critical and most repeated cleaning processes in the fabrication of an integrated circuit (IC). A state-of-the-art IC consists of over 25 masking steps (1), each utilizing a photoresist for pattern generation, and each requiring a subsequent photoresist removal process. Photoresist exposed to processes such as ion implantation and plasma reactive ion etching becomes a heavily carbonized, hardened polymeric residue that can be particularly difficult to remove. Current commercial formulations can be ineffective in removing these etch residues.

Commercial liquids range from organic to aqueous and acidic to basic, but they often share the common property of being environmentally hazardous with regard to flammability, human health, and pollution. In addition, limitations may exist in using liquids to process nanoscale features. For instance, viscosity, surface tension, and diffusivity of liquids may inhibit mass transport and surface wetting.

Carbon dioxide has been suggested as an alternative to traditional liquids for surface cleaning and photoresist development (1). Carbon dioxide is relatively benign in terms of flammability, toxicity, and environmental impact. In addition, CO_2 physical properties include a significantly lower viscosity and surface tension, and a greater diffusivity than liquid counterparts, which suggest the possibility of improving mass transport and wettability. However, carbon dioxide is often a poor solvent in the liquid phase and is even less effective in the supercritical phase. Solubility of materials such as

240
silicones and fluorocarbons is possible, but other materials, especially those with polar moieties, are essentially insoluble.

PHYSICAL PROPERTY MODIFICATION

Due to their unique range of properties, GXLs may overcome the limitations of traditional solvents, pure CO₂, and supercritical mixtures of these components. The physical properties of GXLs range between those of the pure components, suggesting that excellent mass transport and excellent solvent strength are possible. For example, the solvent strength of GXLs is much greater than that of gases or supercritical fluids, while the surface tension and viscosity of GXLs are much lower than those of liquids. GXLs may be tuned for both optimal performance and minimal environmental impact.

Consider a closed system in which carbon dioxide is in equilibrium with a solvent such as ethanol. At low pressures (~ 1 atm), the amount of carbon dioxide that is in the liquid phase is minimal. However, at elevated pressures, carbon dioxide may have significant solubility, and the total volume of the liquid phase will increase (2). This new liquid is termed a GXL. When the pressure is increased to the vapor pressure of the gas, the fluid volume is entirely liquid. Therefore, the composition of the liquid can be varied from that of essentially pure solvent to that of essentially pure liquid CO₂ for miscible materials.

The physical parameters of a GXL as a function of composition can be approximated from pure component data. For example, the properties of an ethanol and CO_2 GXL are considered. The physical properties of these components in Table I gives an indication of the range over which the properties of a GXL may be tuned.

	EtOH	L-CO ₂	units
μ	1.0	.0609	mPa-s
γ	22	1.5	mN/m
ρ	780	500-900	kg/m ³

Table I. The viscosity (μ), surface tension (γ), and density (ρ) of ethanol and liquid carbon dioxide.

Many organic solvents are completely miscible with CO_2 , resulting in a single liquid phase. One such solvent commonly used in microelectronics processing is ethanol. Equilibrium data for this material is plotted in Figure 1. Water, however, is not miscible with CO_2 and therefore cannot be significantly expanded.

Electrochemical Society Proceedings Volume 2003-26



Figure 1. Pressure-composition data for GXLs of CO_2 and ethanol at 18°C, 25°C, and 30°C (2).

Although photoresist residue can often be removed using conventional universal solvents such as ethanol and n-methylpyrrolidone (NMP), some processes such as plasma etching, ion implantation, and thermal annealing yield photoresist residue that can only be removed with more aggressive chemistries. Commercial formulations for these applications primarily contain amines as the reactive component. Therefore, CO_2 expansion of these types of formulations has been investigated. Formulations containing amines yield a precipitate upon mixing with CO_2 , as can be seen upon bubbling CO_2 through the formulation contained in a beaker. CO_2 reacts with the amine to form an insoluble product. This reaction has been reported (3) to proceed as:

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NCOOH$$
 [1]

$$R_1 R_2 NCOOH + R_1 R_2 NH \leftrightarrow R_1 R_2 NCOO^- R_1 R_2 NH_2^+$$
[2]

 CO_2 is clearly not an inert component in these mixtures. Indeed, CO_2 is a Lewis acid, and thus interactions with bases will occur.

While the physical properties of GXLs may lead to improvements in mass transport, the solvent strength of the pure liquid is sacrificed. However, preliminary experiments with GXLs have indicated that the solvent properties of the pure liquid are largely maintained upon expansion. When improvements in transport properties favor a greater transport rate than the corresponding effect of a decrease in solubility, the use of GXLs are expected to be superior to traditional liquids.

Using correlations of physical properties and for mass transfer, the relative dissolution rates as a function of solvent fraction at a particular rotation rate can be predicted. The dissolution rate for a mass transfer limited process is related to the physical properties of the liquid according to

$$DR \propto S \ D^{2/3} \rho^{1/6} \mu^{-1/6}$$
[3]

where S is solubility, D is diffusivity, ρ is density and μ is viscosity (4). The dissolution

Electrochemical Society Proceedings Volume 2003-26

rate will be enhanced due to an increase in diffusivity and a decrease in viscosity of the GXL relative to the traditional liquid if this enhancement has a greater impact on the net dissolution rate than the decrease in solubility.

The tunability of physical properties may also improve compatibility of liquids with materials susceptible to feature collapse and other undesirable interactions. Although highly wetting fluids are desirable for surface coverage, the fluids can also lead to feature collapse and material compatibility problems. Capillary pressures generated within submicron features (5), if sufficiently high, are capable of collapsing the feature. This effect has been reported to occur according to (6)

$$\sigma = \frac{6\gamma\cos\theta_C}{w} \left(\frac{H}{L_w}\right)^2$$
[4]

in which σ is the resulting tensile stress, γ is the surface tension θ_C is the contact angle, w is the line spacing, H is the line height, and L_W is the line width. Each material has a unique critical tensile stress, above which pattern deformation occurs. Feature collapse becomes more of an issue as features sizes are reduced. If the allowable feature size for which lines are fabricated is to be reduced, fluids with reduced surface tensions must be used. While supercritical fluids characteristically have no surface tension, the relatively high pressures that are required to operate under these conditions can be a great disadvantage. Additionally, the poor solvent ability of scCO₂ for many materials will limit its use. An alternative is GXLs, which broaden the range of feature sizes that may be fabricated while the disadvantages associated with supercritical fluids are avoided.

For a highly wetting fluid, the difference between the solid-liquid and solid-vapor interfacial tension is large. However, an additional requirement of processing dielectrics is to maintain the geometry and physical properties of the dielectric. SiO_2 is mechanically and chemically stable, but novel dielectric materials of very different nature may be more sensitive to chemical treatment. Therefore, an additional requirement for a chemical process is that it must leave the properties and geometry of the dielectric unchanged. However, one study has correlated contact angle with solubility of a polymer (7). With few exceptions, solvents that completely wet a polymer will either dissolve or swell the polymer as well. Solvents that do not attack a polymer exhibit a large contact angle (>50°). The tunability of GXLs may be useful for optimizing wetting, collapse, and dielectric compatibility.

PHOTORESIST REMOVAL USING CO₂-EXPANDED LIQUIDS

Thin films were treated in a high-pressure reactor with CO_2 -expanded liquids. Specifically, PHOST samples were dissolved with CO_2 -expanded ethanol. Ethanol is a commonly used solvent in the microelectronics industry and is an excellent solvent for complete dissolution of these PHOST films. Liquid CO_2 , however, does not dissolve these films.

XPS results are shown in Figure 2. For films in which large amounts of residual polymer remain on the substrate, no silicon is detectable and significant charging of the

Electrochemical Society Proceedings Volume 2003-26

surfaces occurs. Silicon is clearly seen on samples with little residue and no shift in the observed binding energy occurs due to charging.



Figure 2. Surface concentration following treatment of PHOST films with GXLs of different composition. Ethanol yields a surface with 20% silicon. The same results are obtained with GXLs containing as little as 25% ethanol. GXLs with less ethanol do not remove the PHOST, and no silicon is detected.

SEM was used to estimate qualitatively the amount of residue remaining on the substrate (Figure 3). These images correspond well to XPS results, in that no residue is visible on samples in which silicon is detected. However, these images also show the nonuniformities that can result from such processes. The observed cracking and peeling of the polymer likely results from stress developed in the film from swelling, although the solubility may be inadequate for complete dissolution of the film. There may be local regions in which ethanol is concentrated and selectively removes the polymer, possibly leading to the voids visible in the film.



Figure 3. The SEM image of PHOST following treatment with CO₂-expanded ethanol at 5.5 MPa and 21°C indicates large amounts of residual polymer on the silicon substrate.

These results indicate that the amount of residual polymer remaining corresponds well with the concentration of ethanol in the liquid, as expected. For low concentrations of ethanol, little polymer is removed, but with up to \sim 75% CO₂ in the GXL, the solvent ability of pure ethanol is maintained. This demonstrates that a solvent such as ethanol may be significantly modified (up to 75%) through expansion with CO₂ while maintaining the solvent ability of the pure liquid.

244

CONCLUSIONS

In this work, dissolution, feature collapse, and dielectric compatibility are discussed as being among those issues which can benefit from tunability of liquid physical properties. The improved transport properties of GXLs relative to traditional liquids may lead to increased dissolution rates. Although weakly wetting liquids can impact total process time and uniformity, strongly wetting liquids will also impact yield. More sensitive film patterns such as high aspect ratio photoresist lines can collapse due to capillary forces. Wetting liquids also may affect the physical properties of a material, particularly the geometry and dielectric constant of a patterned polymer film. If less solvent is consumed, tremendous environmental improvements may be realized without sacrificing performance in photoresist and residue removal processes.

Conceptual demonstration of the use of CO_2 -expanded solvents for photoresist and post-etch residue removal has been performed. Of specific interest are the effects of carbon dioxide, saturated vapor, and gas-expanded liquids upon films such as polyhydroxystyrene (PHOST). These experiments illustrate the tunability of GXLs through the removal of PHOST-based films using CO_2 -expanded solvents. CO_2 expanded ethanol containing up to 75mol% of CO_2 maintains the removal ability of pure solvent. These fluids can therefore be modified to obtain optimal physical properties and ideal ES&H properties.

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245

PHOTORESIST STRIPPING USING SUPERCRITICAL CO2-BASED PROCESSES

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Supercritical CO_2 (SC CO_2) is regarded as an attractive method for photoresist stripping in Back-End-Of-the-Line (BEOL), especially with the introduction of porous low k dielectrics in advanced copper IC devices. The solubility of a deep-UV photoresist (PR) under supercritical carbon dioxide condition was investigated using both solvatochromic and Hildebrand parameters. The main purpose was to evaluate the interactions between photoresist and cosolvent with both parameter models and predict the PR cleaning efficiency of the cosolvents. A process sequence involving a condensation step was also presented and discussed.

INTRODUCTION

Environmental pressure has conducted the semiconductor manufacturing to investigate more environmentally friendly chemicals for PR stripping compared to conventional acid/base/organic solvent blends (1). SC CO₂ -based processes seems the most attractive alternatives in terms of chemical consumption and they have been recognized as an enabling technology, offering the unique opportunity to clean without the drawback of materiel degradation and chemical absorption (reservoir effect) within the porous IC materials (3). In this paper, experimental results, stripping mechanisms, current limitations and potential benefits of SC CO₂ -based stripping were discussed.

SOLUBILITY OF THE PHOTORESIST IN SUPERCRITICAL CO2

Figure 1 shows a conventional stacking profile of a BEOL structure before stripping. The challenges are the complete removal of the Photoresist (PR) "crust" and sidewall polymers without damaging the semiconductor materials, through mechanical, chemical modification and/or contamination. The optimizations of a cosolvent mixture and process condition parameters for PR stripping will be the main focus of this study.

A systematic evaluation of the cleaning efficiency of each cosolvent mixture under various experimental conditions (pressure, temperature and concentration) would require a huge effort. Therefore, the dissolution properties of the CO₂/cosolvent mixtures were compared to the screening of selected numbers of experiments.

Experimental

The solubility was evaluated on a 254 nm positive photoresist (UV5TM from Shipley Co.). A 600 µm thick layer of photoresist was deposited on silicon substrate and soft-baked. The substrate is set in a 50 mm diameter The autoclave. autoclave was pressurized with pure CO2. Then, a homogeneous flow of CO_2 +cosolvent run through the autoclave during a specific time, and finally a pure CO2 flow eliminates cosolvent decompression. before By this method, transition steps of pressure with cosolvent were avoided, so that no precipitation of cosolvent could



Fig. 1: Single-damascene test structure after line etching

occur and false results. The dissolution rate D_r of the photoresist was then obtained by determination of the minimum time for total dissolution of the layer. D_r was determined in pure CO₂ under various conditions of pressure and temperature and also with cosolvents issued from different families: alcohols, ketones, esters and DMSO. DMSO could not be added to CO₂ alone, as its solubility in the working conditions was small. For this reason, a mixture of 2-propanol and DMSO 2/3–1/3 was used.

Evaluation of CO_2 + cosolvent properties

Among the many works published on cosolvency effects in supercritical CO_2 , works of Coutsikos (4) or Sauceau (5), both on the solubility of solid polar materials are of a particular relevance.

Coutsikos proposed to compare the solubility with solvatochromic parameters of the cosolvents. Based on the work performed by Walsh (6), he established that solvation can be due to hydrogen-bonding or charge-transfer complexes. Both interactions can be classified as Lewis Acid-Lewis Base interactions. Therefore, for a Lewis acid solute, the better cosolvent should be a Lewis Base. Solvatochromic parameters α and β are proposed as acidity and basicity strength measurement.

A additional model is the Hildebrand solubility parameter (7). This semi-empirical model is based on Van der Waals interactions between molecules of a liquid. Two materials are expected to be miscible if their Van der Waals interactions are similar, meaning their solubility parameter is similar. This is in fact what happens for low-polarity materials.

Giddings & Al. (8-9) proposed to calculate Hildebrand solubility parameter of a supercritical fluid through equation [1]:

$$\delta_1 = \frac{(a_1)^{1/2} \rho_1}{M_1}$$
[1]

247

where M_1 is the solvent molecular weight and a_1 the intermolecular attraction term of the solvent, obtained by equation [2]:

$$a_1 = \frac{27}{64} \frac{R^2 T_c^2}{P_c}$$
[2]

Equations [1] and [2] are only valid for pure fluids. Sauceau & Al. proposed the following equation to supercritical fluid + cosolvent mixtures (5):

$$\delta_m = \frac{(a_m)^{1/2} \rho_f}{y_1 M_1 + y_2 M_2}$$
[3]

 δ_m is the solubility parameter of the mixture, y_i is the mole fraction of compound *i*, ρ_f the density and a_m the energy parameter of the solvent-cosolvent mixture. The parameter a_m is calculated by using following quadratic mixing rule:

$$a_m = \sum_{i} \sum_{j} y_i y_j a_{ij}$$
 with $a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij})$ and $a_{ii} = a_i$ [4]

where k_{ij} is the binary interaction parameter from Peng-Robinson equation of state (10). The density of supercritical mixture ρ_{f} can be also determined from this equation of state.

Results & Discussion

Solvatochromic and Hildebrand solubility parameters of mixtures and experimental values for PR dissolution rates are summarized in tables I and II and in figures 2 and 3. Parameters of pure liquids and binary interaction parameters were taken from literature (11-13). In order to take into account cosolvent concentration in CO₂, the solubility was correlated to the ratio α / v_i and β / v_i in figure 2 (v_i is the volume fraction of cosolvent).

Solvatochromic parameters. On figure 2, it appears that dissolution results seem to correlate with both parameters α and β of the cosolvents. Solubility of the PR is improved by both acidic and basic parts of the cosolvents. This observation is fully correlating with the well-known efficiency of hydroxylamine-based stripping solvents for this kind of PR. However, this comparison gives only a trend, and an important disparity can be observed.

Pressure (MPa)	Temp. (K)	δ_l (Mpa ^{1/2})	D_r (nm/min)	
180	318	10.9	< 10	
300	323	11.8	< 10	
400	323	12.5	< 10	
500	373	11.1	< 10	
500	473	7.9	< 10	

Table I: solubility parameter of pure CO₂ under various conditions

Cosolvent	α	eta	\mathcal{Y}_i	$\delta_m(\mathrm{Mpa}^{1/2})$	$D_r(nm/min)$
None				10.9	< 10
n-butyl acetate		0	0.070	11.7	53
Methyl isobutyl ketone		0.48	0.073	11.9	64
Methyl ethyl ketone		0.48	0.099	12.2	64
Acetone	0.08	0.48	0.119	12.5	71
Tetrahydrofuran	0	0.55	0.109	12.3	74
Dioxane	0	0.37	0.106	12.5	80
DMSO + 2-propanol (1/3 2/3)	0.50	0.88	0.118	13.0	128
2-propanol	0.76	0.95	0.114	13.0	91
Ethanol	0.83	0.77	0.149	13.1	107
2-propanol	0.76	0.95	0.147	13.6	99

Table II: Cosolvent properties / PR dissolution rate of SC CO₂ + cosolvent (180Mpa; 318K)

<u>Hildebrand</u> solubility parameter. Photoresist UV5TM is a copolymer of 4-tertbutyloxycarbonyloxystyrene and 4-hydrostyrene (TBOC-PHS). The solubility parameter of this copolymer is not known, but by analogy with PS and PMMA, each polymer being about 22.5 MPa^{1/2}, we can assume that the parameter of the photoresist shall remain in the neighborhood of this value. The Hildebrand solubility parameters of SC mixtures are in the range of 11-14, far from PR's value. As illustrated by fig. 3a, at fixed pressure and temperature conditions, an increase of PR dissolution rate corresponds to an increase of δ_l , depending on cosolvent nature and concentration. This means that Hildebrand solubility parameter can be used to evaluate the efficiency of a cosolvent at fixed conditions. But surprisingly, an increase of δ_l of pure CO₂ induced by an increase of its density does not lead to a comparable variation of its solvating power towards PR. So this model is not reliable for the quantitative prediction of PR solubility in CO₂.



Fig. 2: PR dissolution rate vs. solvatochromic parameters of cosolvents

Electrochemical Society Proceedings Volume 2003-26



Fig. 3a and 3b: PR dissolution rate vs. Hildebrand solubility parameter

The two methods were unable to quantitatively predict the cosolvent efficiency, but allowed to provide a reasonable evaluation of their potential performances. However, the dissolution property of CO_2 is weak. Dissolution rate of the PR is about zero in pure CO_2 , even at elevated pressures. The cosolvent effect is not negligible, but the dissolution rate remains one or two orders of magnitude lower than in the pure organic solvents. As illustrated by figure 3b, we can consider that CO_2 + cosolvent mixtures remain at the "foot" of PR solubility curve.

MULTIPHASE STRIPPING

The low dissolution property of supercritical CO_2 is in fact counterbalanced by its uncommon properties to diffuse and transport the chemicals through the organic materials. Also, the solubility property of the SC CO2/cosolvent can be greatly enhanced by the variations of pressure and temperature.

Theory

Partial phase diagram of two selected mixtures (M_A and M_B) were measured by using an optical cell. M_A is composed of $CO_2 + \gamma$ -butyrolactone (mole fraction of γ -butyrolactone is 0.08) and M_B of CO_2 + ethanol + DMSO (mole fraction of ethanol is 0.069 and mole fraction of DMSO is 0.028). Results are presented on figure 4. For M_A , values determined by Q. Xu & Al. are overlaid (14).

At 180 bar and 60°C, M_A is a homogeneous supercritical mixture, with high diffusivity, low surface tension and a relatively low solvent power. If the temperature increases up to 70°C at constant pressure, or if the pressure decreases under 150 bar at constant temperature, retrograde condensation of a liquid phase can be observed. This phase is cosolvent-rich with properties close to the pure solvent under standard conditions, while the remaining supercritical phase is enriched in CO₂.



Fig. 4: Phase diagram of two CO_2 + cosolvents mixtures

This phenomenon was used for PR stripping according to the following sequence:

- Quick diffusion of the supercritical homogeneous mixture through PR's crust (crust is not permeable to liquids!);
- Retrograde precipitation of a cosolvent-rich liquid phase in the photoresist bulk and at the interfaces;
- Fast dissolution of the non-hardened PR under the crust, swelling, cracking and fragmentation of the crust and delaminating sidewall polymers and crust from substrate;
- Carry-over of the residual insoluble materials in the fluid flow.

Figure 5 illustrates intermediate steps during stripping sequence. This multiphase stripping process was able to reduce considerably the process time, wafer in/out process of less than 10 minutes.

Stripping on ULK

A series of experiments were performed on a Methylsilsesquioxane-based porous spin-on dielectric. This ULK has a bulk typical dielectric constant of 2.2. As shown on figure 6, bulk PR was easily dissolved as previously observed for FSG in figure 5. Nevertheless, for small patterns, PR crust was not delaminated. It appeared that adhesion between PR, anti-reflective coating and CMP stop-layer is stronger than for FSG structure. ULK etching process may be the cause of this difference, with an increase of polymerization phenomena and PR hardening.



Fig. 5: SEM pictures of the current SC CO₂ process

CONCLUSION

A potential SC CO₂ stripping process for BEOL was investigated to replace a conventional plasma/wet stripping process. The experimental data showed that the PR dissolution efficiency of a cosolvent mixture under supercritical conditions was diminished compared to standard wet processes. With a concentration of 10 to 15% in the supercritical CO₂, the expected consumption of cosolvents should be in the range of 20 to 50 ml per wafer, depending on the chamber tool size and process conditions. It appears clearly that recovery, regeneration and re-use of the CO₂/cosolvents is fundamental for both cost and environmental issues.

252



DUV resist on ULK, Stripping post Line 1 etch Fig. 6: SEM picture of pattern structure after one process sequence

Further work on multi-phase processes will focus on the applicability and cleaning performance of the SC CO_2 /cosolvent mixtures within a pre-industrial tool platform.

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Electrochemical Society Proceedings Volume 2003-26

POST-ETCH CLEANING OF 300MM DUAL DAMASCENE LOW-K DIELECTRIC STRUCTURES USING SUPERCRITICAL CO₂

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ABSTRACT

Supercritical carbon dioxide (SCCO₂) has recently been introduced as a potential solution to many challenges currently on the semiconductor processing industry's roadmap. Unique attributes such as zero surface tension, liquid-like density and gas-like viscosity give SCCO₂ an early edge over currently utilized cleaning techniques. Applications of SCCO₂ in solution with various chemical mixtures (co-solvents) are discussed for wafer piece development and full 300mm wafer processing, focusing on the removal of post-etch polymer and remaining photoresist from dual damascene structures in low-k ILD material.

INTRODUCTION

As the microelectronics industry continues to improve performance, decrease power consumption and overcome obstacles that threaten to inhibit success, process engineers are, in turn, challenged to invent new materials, designs, and manufacturing processes. Changes in stack materials, photoresists, and integration schemes often require changes to "standard" semiconductor manufacturing processes. Some of these changes can be accommodated with current processing technologies, tools, and chemistries. Others, like novel material introductions or high aspect ratio/shrinking pitch features, may require new "enabling" solutions. Over the last 30 years the semiconductor industry was enabled primarily through advances in equipment design and through process changes that provided scaling (ongoing reduction of feature sizes). Recently, increased numbers of new materials, integration schemes, high aspect ratio structures, and features with tighter pitch and smaller CD's are pushing the limits of current processing techniques and may require unique, "enabling" solutions to meet these challenges, not simply the next generation of equipment. Wet etch and cleans processes are present in almost every patterning step and, hence, are exposed to almost every material in the semiconductor manufacturing process flow. Successful implementation of process flow changes can often hinge on wet etch compatibility. Therefore, wet etch and cleans engineers must continue to develop new technologies, chemistries, applications, and solutions to enable new ideas across all process modules.

Increasing aspect ratios, new materials (and interfaces), selectivity, and continuously shrinking dimensions look to be the key technical process challenges for wet etch and cleans modules in the foreseeable future. In order to keep pace with these

Electrochemical Society Proceedings Volume 2003-26

changes, unique, enabling cleaning solutions will be necessary. Wafer cleaning with supercritical carbon dioxide (SCCO₂) is an example of a novel cleaning technology, which could solve many future roadblocks currently on the horizon for wet etch processes [1,2]. SCCO₂'s liquid-like density, gas-like viscosity, and zero surface tension offer an increased opportunity to clean out smaller dimensions in future semiconductor structures [3,4].

The liquid-like density of SCCO2 is suitable for the dissolution of various small molecules like co-solvents or other solutes that has aided its use for caffeine extraction, polymer applications and recently in the pharmaceutical industry due to its benign nature and very high selectivity. Further, the increased ability to tune the density of carbon dioxide above its critical point (in the supercritical state) permits manipulation of the phase behavior of the system to meet specific application needs. The ability to utilize an anhydrous-chemistry system provides further advantages over many traditional aqueous cleaning systems that can leave water behind in porous media leading to future dielectric (ILD) damage and/or increased capacitance [5]. Specifically, to micro-electronic applications, SCCO2 would lend itself viable through niche applications wherein its selectivity, high diffusion rates, flowable nature at high velocities, ready miscibility with gases, and hydrocarbon-like properties resulting in potential moisture-free wafer processing would play a huge role [6].

A key challenge in back end of line (BEOL) integration is to reduce the dielectric constant (k) of the inter-layer dielectric (ILD) films so that cross talk between metal lines can be minimized. In general, as the k-value of an ILD is reduced, the materials become more porous, fragile, and susceptible to damage by traditional etch and cleans processes. The purpose of this study was to determine if SCCO₂-based cleaning solutions could replace prevailing post-etch/ash and immersion/spray cleaning processes. A review of the work using SCCO₂ based solutions as cleaning agents for BEOL post-etch cleans on 300mm low-k substrates is presented.

DEVELOPMENT RESULTS

Approach:

The study followed two main methodological phases for development. Phase 1 was performed on a bench top tool, where wafer piece experiments were performed on a host of substrate/chemistry combinations, and phase 2 was conducted on a 300mm tool, where whole wafers were processed for chemistry solutions initially successful at the chip level. Bench top learning provided useful feasibility data that was used as a platform to develop full-wafer clean processes on the 300 mm tool. Successful transfer of solutions from bench top to 300mm tool was not always straightforward and uncovered process dependencies on the materials being cleaned, process chamber conditions, and the composition and volumes of co-solvents chosen. Co-solvent/chamber material interactions, chamber conditioning procedures, and the accuracy of small volumetric measurements impacted cleaning performance and affected the breadth and robustness of the final available process windows. SCCO₂-based co-solvent systems also suffer from

Electrochemical Society Proceedings Volume 2003-26

fluid flow and chemical loading challenges equivalent to those in traditional wet etch fluid systems. Center to edge, or chamber location specific processing differences can occur (Figure 1) and must be taken into account. In general, the process concerns and development approach of applying $SCCO_2$ to clean post etch substrates is similar to strategies that are employed for new chemical applications with existing industry systems like spray or immersion based tools.



Figure 1. Center-to-Edge cleaning variances due to flow and chemical loading can be seen in traditional wet cleaning methods as well as SCCO₂-based systems.

Experimental:

 $SCCO_2$ was evaluated in combination with cleaning solutions. In generic terms these solutions could be composed from one or more active chemicals, inert chemicals, and co-solvents. Total chemical volumes per wafer ranged from 10mL/wafer to 100mL/wafer; an accuracy of $\pm 0.1~\mu L/wafer$ for some materials was required to ensure appropriate process window for some applications. Individual wafer chips were inspected visually with an optical microscope and by SEM. Full wafer process runs afforded additional inspection techniques including automated defect analysis and electrical testing as available.

The structures assessed were dual damascene vias and trenches etched into a variety of ILD materials ($2.2 \le k \le 3.0$), listed in Table I. The task was to remove all remaining photoresist, ARC material, and etch-induced polymer from the wafer without damage to the ILD structures being cleaned. Copper compatibility and a high selectivity (>20:1) to materials at the bottom of via structures was also a requirement for success. Processing conditions for all trials (chip and full wafer) consisted of pressures between 1000-3000psi and temperatures between 40C and 70C. Plasma etch processes used to create the dual damascene ILD structures were not modified to accommodate for known SCCO₂ cleaning strengths or weaknesses.

Electrochemical Society Proceedings Volume 2003-26

Results:

SCCO₂-based solutions were found effective in removing etched or unetched bulk photoresist in all cases. Depending on the etch chemistry utilized and, consequently the chemical makeup of the resulting polymer layer, the increased diffusivity of the SCCO₂ / co-solvent mixture was manifested by the etching of bulk photoresist and underlying ARC layers without removal of the outer, post-etch crust. In some material applications this property can assist the cleaning process by providing a greater surface area for future chemical attack or a weaker material integrity for mechanical cleaning (e.g. sonication or spray), while for other applications, the increased diffusivity could lead to failure modes such as interface delamination.



Figure 2. Bulk Photoresist and ARC material removed from via and trench ILD structures using SCCO₂-based cleans. Post-etch polymer crust remaining.

Removal of the post-etch polymer crust, without damage to the underlying ILD, was a specific challenge for the SCCO₂-based cleaning trials. Etch processes utilizing primarily fluorocarbon gas mixtures leave behind a polymer composed of Si, O, C, F, during plasma etch of SiO₂-based ILD materials. Oxidation, in the form of plasma based ash or wet chemical treatments, can assist in the removal of this polymer, but often these process additions results in ILD damage as well. Application of SCCO₂-based co-solvent mixtures to remove this polymer crust most often required the use of oxidation techniques that did not provide a clear advantage over traditional wet cleaning techniques on the materials tested in this study.

Samples exposed to the post-etch plasma ash process that broke down the resilient polymer crust could also be cleaned using SCCO₂ based clean solutions. This specific process flow also appeared to provide distinct advantages over traditional cleaning methods. The limited amount of relatively concentrated chemistry and relatively short exposure times often reduced the ILD damage observed with standard immersion or spray solutions. The removal of residues from the bottom of vias was dramatically improved in some applications using SCCO₂-based mixtures, see Figure 3.



Figure 3. Porous CVD CDO Via Structures cleaned with SCCO₂-based co-solvent mixture.

These advantages become important as aspect ratios increase and dimensions decrease. Experimentally these advantages were witnessed in cleaning a lightly-porous, (~5-10%) PECVD CDO (Carbon-doped oxide) k~3.0. In this example, via resistance increased in the standard cleaning trials due to improper removal of post etch residues, low etch selectivity, and cross-wafer variances (Figure 4). Attempts to improve this process using standard cleans led to increased ILD damage. Figure 5, shows a successful application of SCCO₂ and co-solvents to properly clean the wafers which were able to be re-inserted into a 300mm production fab for subsequent processing and provide electrical testing data similar to that defined by the control group.



Figure 4. Normalized via chain resistance plot showing SCCO2-based cleaning improvements over immersion cleaning methods for a particular integration scheme as well as a predictable behavior compared to reference data (control).

Electrochemical Society Proceedings Volume 2003-26



Figure 5. CVD CDO (k~3.0) Dual Damascene structures cleaned with a SCCO₂-based co-solvent mixture. Left photo is pre-cleans, right photo is post-cleans.

While investigating the materials listed in Table 1, SCCO₂-based solutions were tested in parallel with standard cleans solutions. Our experience revealed that as the material stacks became more complex or the materials became more porous, SCCO₂-based co-solvent solutions began to show advantages in etch selectivity over standard immersion or spray cleans options. Reductions in active chemistry volumes and application times as well as the inert nature of SCCO₂ to the more fragile materials reduced collateral damage to ILD structures and underlying materials on the wafer during cleaning. Figure 6 shows a successful SCCO₂-based cleans process for removal of 248nm photoresist, an SiO₂-based ARC layer, and post-etch polymer from a highly porous SiO₂-based ILD, NanoglassE.

	PR	Post-etch	ARC/
		polymer	Via Fill
SiOF	Yes	Yes	Yes
NanoglassE	Yes	Yes	Yes
p-SiLK	Yes	Yes	N/A
CVD CDO 1	Yes	No	Yes
(k~2.5)		(Yes, if ashed)	
CVD CDO 2	Yes	No	Yes
(k~3.0)		(Yes, if ashed)	

Table I. Post-Etch Cleans Material Test Matrix.





CHALLENGES AHEAD FOR SCCO2

While post-etch cleaning with $SCCO_2$ has shown some unique signs of promise, development with this technology has many similarities to current wet chemical processing techniques. Bench top development with small chemical quantities and wafer pieces does not always transfer easily to full wafer processing tools. Process parameters such as fluid flow, temperature uniformity, chamber material interactions and chemical loading are valid concerns to $SCCO_2$ -based cleaning, just as they are in current cleaning technologies such as immersion or spray systems. The process windows were found to be huge in some applications, while impossibly small in others. The complete cleaning process relies both on mechanical removal as well as dissolution, depending on the task at hand. Production systems must be able to efficiently filter particulates and films from the fluid flow without redistributing them across the wafer, see Figure 7.



Figure 7. Particles and films dislodged during SCCO₂-based cleaning processes must be filtered out to avoid yield degradation. This is not unique to SCCO₂-based cleaning and is meant to display only the state and size of particles to be filtered during the cleaning process.

Electrochemical Society Proceedings Volume 2003-26

 $SCCO_2$ -based cleaning systems must also overcome challenges unique to highpressure systems. High pressure metal-metal sealing surfaces required in current $SCCO_2$ systems generate metallic particles that can present potential contamination as well as defect-related yield issues in a semiconductor processing environment. Co-solvent chemical properties and their interactions with materials in $SCCO_2$ environments are making advancements, but are not widely understood. High-pressure systems (3000+psi), while not new to the world, are new to the semiconductor industry and the safety systems therein. Successful implementation of this technology will require transfer of unique process capability as well as the safety knowledge associated with these systems. Further study at both the academic and industrial levels of $SCCO_2$ safety, process, and the chemicals and materials in contact with it are key to the advancement of $SCCO_2$ applications.

SUMMARY AND CONCLUSIONS

Cleaning of BEOL post-etch residues with $SCCO_2$ has the potential to break down barriers currently projected on the wet etch process horizon for semiconductor manufacturing applications. $SCCO_2$ is a unique fluidic system in which small volumes of chemistry can be applied to structures and interfaces which are difficult to reach with common technologies today. $SCCO_2$'s inert relationship to most porous, low-k materials makes it an especially attractive cleaning medium for these materials. Results presented herein have shown that proper application of $SCCO_2$ along with co-solvent chemistries can deliver acceptable cleaning performance on certain 300mm low-k dual damascene BEOL post-etch wafers typical of the 90nm and 65nm technology nodes. Full 300mm wafers were cleaned using a $SCCO_2$ -based co-solvent cleaning system and continued through a production cleanroom environment to downstream processing steps where electrical test results showed performance equal to or better than wafers cleaned with known immersion clean solutions.

SCCO₂-based cleaning is still in its infancy, however, and has yet to find a clear, enabling niche in the semiconductor cleaning space that cannot be fulfilled by current cleaning technologies. The industry will adopt new tool and process changes for enabling solutions when the data, scientific understanding, and safety awareness surrounding the changes support the need for a disruptive technology. The process tools are maturing, but still have obstacles to overcome in order to meet the high-yield requirements of competitive production fabs. For SCCO₂ to successfully transition into the semiconductor fab environment, the continuing scientific efforts by academia and industry need to provide additional understanding into this novel application on the fronts of chemistry, materials, and safety.

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IMPACT OF PHASE BEHAVIOR ON PHOTORESIST REMOVAL USING CO₂ BASED MIXTURES

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ABSTRACT

In order to better understand the mechanism of photoresist removal, phase behavior studies were performed on CO₂-based mixtures. Solutions of tetramethylammonium bicarbonate (TMAHCO₃) in methanol were used as co-solvents with CO₂. The phase behavior of this mixture studied at temperatures between 25 and 70 °C and was TMAHCO₃/CH₃OH mole ratios of 0.127 and 0.02 by using a variable volume high pressure cell. Photoresist removal was performed under different phase conditions and the removal efficiencies compared and contrasted. Blanket plasma deposited fluorocarbon films were used to investigate the removal mechanism. The removal process was reaction rate limited and depended on the temperature and active species Compatibility tests on plasma deposited SiO₂ and concentrations. CORAL[™] low-k dielectric material were carried out both at atmospheric and elevated pressures.

INTRODUCTION

The demand for faster and more reliable microelectronic devices has led to feature size reduction and the incorporation of new materials (e.g., low-*k* dielectric materials and copper for metallization) into process sequences. In modern IC manufacturing, cleaning procedures account for approximately one-third of the production steps. Presently, the etch residue is removed by 'ashing' in an oxygen plasma, thereby converting the polymeric residue to volatile products¹⁻². However, this method is not completely effective when non-volatile species such as metals and inorganic species are present, and can cause radiation damage and resist 'popping'². An additional liquid step is subsequently used to remove the residue completely.

Due to the limitations of plasma processes, liquid-based methods continue to be prevalent in integrated circuit (IC) fabrication. Current liquid-based methods for post etch cleaning that employ commercial formulations based on hydroxylamine solvents or fluoride based chemistries³⁻⁵ (semi-aqueous chemistries or SACTM), possess compatibility limitations, and in addition, may result in unacceptable levels of critical dimension (CD) loss⁴. In addition to being incompatible with organic groups in the dielectric materials, these wet processing steps also use large amounts of de-ionized water and isopropyl alcohol (for drying). Additionally, liquids may be inhibited from entering small, high aspect ratio features. Moreover, if entry into small vias and trenches does occur, transport

Electrochemical Society Proceedings Volume 2003-26

of liquid and associated residues or contaminants out of the high aspect ratio features will be difficult. Finally, the interfacial forces generated when trapped fluid dries within the small via or trench, can cause the microstructures to collapse and $stick^6$.

The above issues demonstrate the need to develop environmentally and substrate compatible, cost effective and efficient photoresist and post plasma etch residue removal technology that decreases solvent use. Carbon dioxide-based mixtures are of interest in microelectronics fabrication⁷⁻⁸ due to the easily attainable critical temperature and pressure, non-flammability, availability, environmentally benign nature, and low cost of CO_2 . Unfortunately, supercritical CO_2 alone is unable to remove photoresist or post etch residues; thus all reported processes invoke the incorporation of various co-solvents (such as propylene carbonate (PC)⁹, dimethyl sulfoxide (DMSO), acetyl acetone, acetic acid, etc¹⁰). However, additional complexity can arise from co-solvent incorporation into carbon dioxide, since various reactions such as those between acids and bases and salt formation can occur. Furthermore, because co-solvents may display dissimilar phase behavior to that of CO_2 , more than one fluid phase may be present in these mixtures at the temperatures and pressures used in photoresist removal processes.

This study demonstrates the influence of phase behavior on the cleaning ability of near critical CO_2 based fluids. Indeed, high temperatures/pressures may be necessary to attain the supercritical state in CO_2 modified with co-solvents. In such cases, a single phase (usually liquid) may result at moderately high pressures. Such liquid mixtures may possess a desirable combination of superior transport properties and high solvent strength (higher density than supercritical fluids). Recently, we demonstrated that tetramethylammonium hydroxide (TMAH) is an efficient basic additive in the CO_2 co-solvent mixture due its ability to attack the plasma-generated photoresist crust¹¹⁻¹³; in addition, reactions between TMAH and CO_2 were studied in detail¹². In this work, we report on photoresist and post etch residue removal using such CO_2 -rich liquid mixtures, and correlate the removal ability using these mixtures with their phase behavior.

EXPERIMENTAL

Phase behavior data was obtained using a variable volume high-pressure cell (Figure 1)^{14,15}. All fluid treatments were performed in a high pressure view cell reactor¹³ on substrates (supplied by Novellus Systems, Inc.) containing residues from etching a low-*k* film (CORALTM) in a fluorocarbon-based plasma. The film stack and associated thicknesses of the layers are shown in Figure 3a (sample before treatment). Silicon substrates with thin fluorocarbon films (supplied by Air Products) were subjected to similar treatments to better understand the mechanism of residue removal. Samples were characterized with a PHI Model SCA 1600 X-ray photoelectron spectrometer to determine surface composition and bonding configurations.

Compatibility tests on plasma deposited SiO_2 and $CORAL^{TM}$ low-*k* dielectric material were carried out at both atmospheric and elevated pressures. Spectroscopic ellipsometry was used to measure the thicknesses change of SiO_2 and $CORAL^{TM}$.

Electrochemical Society Proceedings Volume 2003-26



Figure 1. Schematic diagram of the view cell and experimental apparatus used for phase behavior measurements.

Tetramethylammonium hydroxide (TMAH, 25 wt%) in methanol, and methanol (HPLC grade) were obtained from Aldrich, Inc. Tetramethylammonium bicarbonate was prepared by bubbling CO_2 through TMAH at atmospheric pressure until a clear solution (no precipitate) was obtained¹². The presence of bicarbonate was confirmed by titration with calibrated HCl solution. Carbon dioxide (SFC grade, 99.9999% purity) was supplied by Airgas.

RESULTS AND DISCUSSION

Recently we demonstrated that photoresist and plasma etch residues can be removed by adding a TMAH-CH₃OH mixture to sub- and supercritical CO_2^{11-13} . However, incorporation of TMAH into CO_2 required an understanding of the interactions between all components. As a result of acid-base reaction between acidic CO_2 and basic TMAH solution¹³, the carbonate salt is produced initially; however, in an excess of CO_2 , the bicarbonate is formed and the precipitate ([(CH_3)₄N]₂ CO_3) dissolved:

$2(CH_3)_4NOH + CO_2 \rightleftharpoons [(CH_3)_4N]_2CO_3 + H_2O$	(1)
$[(CH_3)_4N]_2CO_3 + H_2O + CO_2 \rightarrow 2(CH_3)_4NHCO_3$	(2)

As a result of reaction (2) the bicarbonate salt, rather than the TMAH solution is the active ingredient in photoresist and etch residue removal at elevated pressures in this mixture. In the current work, we investigate possible correlations between the cleaning ability of the bicarbonate- CO_2 mixture and its phase behavior.

Phase Behavior

The phase behavior of CO_2 -TMAHCO₃ mixtures at 70 °C was explored with two different molar ratios of bicarbonate-methanol in the co-solvent. The phase behavior of the original solution (25 wt% in methanol corresponding to a TMAH/CH₃OH mole ratio of 0.127, solid circles) and the solution after dilution with methanol (TMAH/CH₃OH of 0.02, open circles) is shown in Figure 2. For comparison, the phase behavior of a

265

TMAHCO₃ solution prepared *a prior* by bubbling CO₂ through the solution of TMAH at atmospheric pressure is presented on the same plot (solid and open squares). An increase (~10 °C) in the mixture temperature was observed upon first addition of CO₂ to the original solution of TMAH at elevated pressure, indicating the exothermic nature of the reaction. An analogous temperature rise was observed during the preparation of TMAHCO₃ solutions at atmospheric pressure. The similarity in phase behavior for both mixtures supports our initial assumption that TMAHCO₃, rather than TMAH is an active ingredient in photoresist and etch residue removal at elevated pressures.

With increasing concentrations of bicarbonate, the bubble point pressures increase due to the larger concentrations of ionic species. At 40 mole% CO_2 , the pressure necessary to move from the dual phase region to a single phase exceeds 3050 psi. However, it is evident from Figure 2 that at 3050 psi, a single phase can be obtained with diluted bicarbonate solution with up to 71 mole% CO_2 . The phase region at CO_2 mole fractions below 30% is of little interest since it does not result in a significant reduction in co-solvent usage during cleaning processes.

Cleaning efficiency

Diluted bicarbonate solution was used to obtain single phase mixtures while the (as formed) bicarbonate solution was used to obtain two phase mixtures. In both two phase (treatment A, Fig.2) and single phase (treatment B, Fig.2) experiments, the mole flow rate of TMAHCO₃ was kept constant (0.0262 mole/hr).



Figure 2. Experimental isotherms: •- TMAH/MeOH=0.127; •-TMAH/MeOH=0.021; **-** TMAHCO₃/MeOH=0.127; -- TMAHCO₃/MeOH=0.02. A -treatment performed in two phase region; B -treatment performed in single phase.

Initially, the cleaning efficiency was studied as a function of phase state at 70 $^{\circ}$ C, with a cleaning time of 45 min. At this temperature and cleaning time, the residues were completely removed under both single and two-phase conditions. As an example, Figure 3 shows the SEM images of a 250 nm via structure before and after cleaning.

Electrochemical Society Proceedings Volume 2003-26



(a)

(b)

Figure 3. SEM images of a) sample before treatment: i) 400 nm photoresist residue and BARC ii) 50 nm SiO₂ iii) 500 nm CORALTM iv) 50 nm SiC; b) sample exposed to two phase CO₂-CH₃OH-TMAHCO₃ mixture.

Since the phase transition pressure depends on temperature, the phase behavior studies were performed at 3 different temperatures for the diluted bicarbonate solution. The phase behavior of the diluted bicarbonate system rather than the original bicarbonate solution was investigated as a function of temperature because: i) the single phase can be achieved upon addition of a high mole fraction (> 60%) of CO₂ at moderate pressure; ii) at room temperature and higher salt concentrations, addition of CO₂ resulted in the formation of a solid phase, which was not soluble upon further CO₂ addition; further increase of pressure resulted in additional precipitation. The expected decrease in the phase transition pressure with a decrease in temperature was observed.

In order to investigate the cleaning efficiency of the mixture, the flow rates of cosolvent were fixed and the temperature varied. Due to the change in density of CO₂ as a function of temperature, the compositions of the mixtures A and B change slightly; compositions are listed in Table I. The effect of temperature on residue removal in single and two-phase mixtures is shown in Figure 4. Clearly, for both cleaning conditions the results are similar - complete removal occurs only at temperatures above 50 °C. These results suggest that the residue removal is reaction limited at lower temperatures. The dotted line in the Figure 4 represents the reference point for a clean sample; XPS Si%>22% implies that the sample is clean according to correlations with SEM inspection^{11, 13}. The single phase mixtures result in somewhat improved cleaning efficiency (higher Si%) at all temperatures investigated.

To investigate the removal mechanism, plasma deposited unpatterned fluorocarbon samples were used in cleaning experiments. If chemical attack of the fluorocarbon film by the CO₂-bicarbonate mixture occurs and removal is reaction limited, a change in F:C ratio as a function of temperature is expected. Thus, the fluorocarbon films were exposed to both single and two phase mixtures at two different temperatures; $25 \,^{\circ}$ C and $70 \,^{\circ}$ C were chosen to accentuate the changes in F:C ratio.

Table I. Composition (mole%) of the mixtures used in cleaning experiments at various temperatures. The mole flow rate of TMAHCO₃ was constant (0.0262 mole/hr).

	Mixture A			Mixture B		
Temperature	CO ₂	TMAHCO ₃	Methanol	CO ₂	TMAHCO ₃	Methanol
25 °C	94.37	0.59	5.04	75.93	0.47	23.59
50 °C	93.53	0.68	5.79	73.31	0.52	26.17
70 °C	92.47	0.79	6.74	70.32	0.58	29.10

In order to verify the effect of bicarbonate on residue removal, a fluorocarbon film was exposed to CO_2 only at 70 °C and 3000 psi (control sample). All treatments were performed for 15 min. Figure 5 shows that at 25 °C, addition of bicarbonate in single or two-phase mixtures does alter the F:C ratio.



Temperature(^OC)

Figure 4. Comparison of cleaning efficiency at different temperatures. Treatment A (two phase): 3000 psi, flow rate 11 mL/hr (TMAHCO₃/CH₃OH=0.127); Treatment B (single phase): 3200 psi, 55 ml/hr diluted bicarbonate solution TMAHCO₃/CH₃OH=0.02). T=70 °C.

These results confirm our previous assumption that attack of the photoresist crust is kinetically limited. At 70 $^{\circ}$ C, a significant reduction in F:C ratio was observed with the single phase mixture but no change relative to the control sample was observed with the two-phase mixture. Such results imply that at constant mole flow rate, the single phase mixture is more efficient with respect to chemical attack of the fluorocarbon film than is the two-phase mixture. This is consistent with the fact that in a two-phase mixture, the bicarbonate concentration in the vapor phase is expected to be orders of magnitude lower than the concentration in the liquid phase. Thus, when a sample is exposed to the two phase mixture, the amount of bicarbonate that contacts the sample surface is much lower than in the single phase mixture. These results were confirmed by investigation of the minimum time required for complete residue removal; a shorter time was needed for a single phase mixture relative to a two phase mixture.

268



Figure 5. Change in F:C ratio after exposure of blanket fluorocarbon films to two phase and single phase mixtures at 25 °C and 70 °C.

Compatibility tests

Compatibility of the above cleaning mixtures with microelectronic materials is critical in state-of-the-art device fabrication and represents one of the driving forces for this study. Compatibility of our cleaning mixtures was extensively tested on blanket films of plasma-deposited SiO₂ (capping film) and CORALTM (low-*k* film). SiO₂ etched slowly (0.2 nm/hr) during exposure to the two-phase cleaning mixture. However, the CORALTM thickness was not changed by exposure to either single or two phase cleaning mixtures at elevated pressure. In contrast, the bicarbonate liquid mixture etches SiO₂ at 0.55 nm/hr at 50 °C and atmospheric pressure. Thus, the CO₂ based mixtures remove some of the drawbacks associated with liquids while preserving their cleaning ability at moderate temperatures and pressures.

CONCLUSIONS

Post plasma etch residue removal efficiency was investigated as a function of elevated pressure cleaning mixture phase state. The phase behavior of the CO_2 -CH₃OH-TMAHCO₃ system was studied at different temperatures and bicarbonate concentrations. At a fixed mole flow rate of additive, the single phase cleaning mixture demonstrates higher removal efficiency than does the two phase mixture. To achieve full residue removal with the two phase mixture, longer treatment times and higher flow rates are required. In both cases, the cleaning procedure is kinetically limited and no cleaning occurs at temperatures below 50°C. Plasma deposited fluorocarbon films were used to investigate the removal mechanism. No change in F:C ratio is observed during exposure to two-phase mixtures at 0.0262 mole/hr flow rate. However, the increase in flow rate results in a significant drop in F:C ratio, implying that chemical attack of the fluorocarbon takes place. The difference in removal efficiency as a function of phase state can be attributed to the concentration of reactive material that contacts the residues.

Electrochemical Society Proceedings Volume 2003-26

Use of single phase mixtures facilitates easier transport of active species to the surface. Both single phase and two phase mixtures demonstrate high compatibility with plasma deposited SiO_2 and $CORAL^{TM}$.

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COPPER LOW-K CONTAMINATION AND POST ETCH RESIDUES REMOVAL USING SUPERCRITICAL CO₂-BASED PROCESSES

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ABSTRACT

Cleaning processes, especially copper contamination removal, have become critical for the porous ultra low-k (ULK) integration in modern IC fabrication and their detrimental impacts are deemed critical for the ULK and overall performances of the devices. Therefore, new cleaning processes are developed which have to be efficient enough to remove the Cu contamination and the post etch-residues while preserving the Cu lines and the ULK materials. Supercritical CO₂-based treatments (SC CO₂) provide a promising alternative method due to its unique characteristics of both a liquid and a gas compared to conventional cleaning processes (1). In supercritical state, CO_2 is a media able to transport active chemistry within the porous ULK matrix without damaging the material. In this paper, Cu-residues trapped within a porous UKL were removed with an efficiency of more than 99% and copper PER residues on patterened devices were removed selectively and without significative damage of the material stack after process optimisation.

INTRODUCTION

Device dimensions scaling down to the 0.09 μ m range requires the integration of porous low-k dielectrics and improvements in cleaning technology particularly at the end of via etching, as copper is sputtered from the underlying copper line onto the sidewalls of the dielectric stacks. New methods are required to remove this contamination which have to be efficient, compatible with ULK, and selective between oxidized and metal copper. Indeed, this cleaning targets the removal of: (i) Cu contamination trapped inside ULK bulk, (ii) post etch residues and (iii) the copper oxidized layer on Cu lines. SC CO₂ processes appear to be an attractive solution because of its capacity to decontaminate even within the ULK matrix. Figure 1 shows SIMS analyses of a SC CO₂ cleaning on copper contaminated ULK film compared to a reference wet clean. This result emphasized the limitation of wet technologies to remove copper residues trapped within the porous low-k material whereas SC CO₂-based treatment was efficient to decontaminate the ULK.

Electrochemical Society Proceedings Volume 2003-26



Figure 1: SIMS analyses showing copper contamination level vs ULK thickness.

EXPERIMENTAL

After dielectric etching it was demonstrated that for the 0.25 μ m technologies, Cu contamination on backend dielectrics can be very high (1^E14 to 1^E16 at/cm²). It was advised that a residual Cu level under 1^E13 at/cm² at the insulator's surface and sidewall interfaces and lower than 1^E11 at/cm² range on the backside were necessary (2). With the aim of studying Cu residue cleaning in similar conditions, different copper species including Cu(0), Cu(I) and Cu(II) bulk and surface types were investigated at an equivalent Cu level range:

- in order to study post etch residues (PER) removal SC CO₂ cleaning processes were tested on damascene structures. In this case, the cleaning efficiencies were evaluated by SEM observations.
- to analyze accurately Cu decontamination on and within the ULK matrix, a similar cleaning study was carried out on blanket wafers. The samples were covered with a 3000Å thick ULK and intentionally contaminated with metallic copper at a level of a few ^E15 at/cm² using CVD. Some of the contaminated wafers were then exposed to ozone in order to oxidize part of Cu(0) into CuO and Cu₂O. The quantitative determination of copper contamination in the material before and after SCCO₂ cleaning was performed by Vapor Phase Decomposition-Atomic Absorption Spectroscopy (VPD-AAS): AAS analysis the total Cu contamination after the complete decomposition of the native SiO₂ and ULK film by VPD.

Usually, efficient metal extraction in SC CO₂ is achieved with diketone compounds as chelating agents. Also a solvent is mostly employed to improve the chelating agent solubility in SC CO₂: ethanol is largely used because of its high solubility in SC CO₂ (3). Besides, the use and ability of the diketone, hexafluoroacetylacetone (hfac), to chelate copper under SC CO₂ for microelectronic cleaning applications, has been previously discussed by B. Xie et al. (4). Consequently, all extraction mixtures tested in this study were balanced against a CO₂/hfac/ethanol cleaning mixture. In addition, fluid pressure and temperature are essential parameters which compete with each other since the fluid density and extraction kinetic are directly related to them (3). In this study, the cleaning procedures were performed in a SC CO₂/solvent/chelating agent mixture at 50°C and 180 bar under static conditions except for the charging and purging of pure CO₂.

COPPER DECONTAMINATION

It was suggested that the efficiency of the SC $\rm CO_2/additives$ cleaning process depended on several parameters :

- On the one hand, the chemical reaction kinetic between copper residues and SC CO₂/additives would influence the extraction time and the choice between dynamic or static conditions. Different process times were tested, and the results demonstrate that a 5 min static treatment can reach a cleaning efficiency greater than 99% (cf. Figure 2).
- On the other hand, efficiency of SC CO₂/additive mixtures would be influenced by the individual concentration ratios of additives on the quantity of copper residue removed. We have checked that the amount of chelating agent is several hundred times higher than the amount of Cu atoms present on the samples. Thus, given the high diffusivity of supercritical fluids, this concentration is not a limiting parameter.
- Furthermore, the molecular structure of the chelating agent can have an effect on the chelation mechanism and thus on the cleaning efficiency.
- Finally, the chelation performance in SCCO₂ can be altered by the poor dissociation effect of CO₂ and a lack of solubility of the additive within the solvent and/or CO₂.



Figure 2: Remaining Cu contamination vs cleaning time by hfac/ethanol dissolved in SC CO₂.

Influence of the chelating agent structure

In order to understand chemical mechanisms taking place between the CO_2 , co-solvent, additives and copper / copper residues at high pressure, and to choose an efficient extraction mixture, copper decontamination measurements of a wide range of organic chelating agents in SC CO_2 were carried out on copper contaminated ULK films. Also, the two first parameters previously proposed were chosen for not being limiting factors of the cleaning: 5 min static process at a chelating agent concentration of about 1000 ppm in CO_2 . From literature results, this investigation was undertaken on diketone additives (3). The two ketone groups were placed at different positions from one another on the hydrocarbon backbone in order to identify the optimal molecular structure(s). The analysis demonstrated that two classes of diketone chelating agents (including hfac) can remove efficiently copper contamination from ULK matrix under supercritical conditions (cf. Figure 3).

Moreover, it was found that substitution can modify slightly the electron charge density within the carbon between the two ketone groups. Thus, it can alter the equilibrium between the enol and keto forms of the β -diketones (cf. Figure 4) which appeared to have an important role in metal complexation and on the chelation selectivity between copper and copper oxide species (5). Also, the enol/keto ratio can be tuned by the co-solvent properties (dielectric constant) and the process conditions (pressure and temperature), in order to promote the enol form which accelerates formation of the metal chelate (6).



Figure 3: Cu decontamination efficiency results of different copper chelating agents dissolved in SC CO₂.



Figure 4: keto/enol equilibrium of β -diketones.

Results on copper decontamination with hfac as a chelating agent and different solvents suggested that ethanol (k-value: 24,3) is polar enough to shift the equilibrium toward the enol form (cf. Figure 5). However, keto/enol equilibrium alone could not not explain all these results: another parameter seemed to have an influence on chelatation mechanisms (such as the available water quantity in the mixture (4)). So, subsequent work is required to have a better understanding of the mechanisms involved during the cleaning under supercritical conditions, and further optimize the formulations for this new cleaning technology.



Figure 5: Cleaning efficiency of CO₂/hfac/solvent cleanings vs solvent dielectric constant.

Influence of solubility of the additive within the solvent and/or CO2

In addition, SC CO₂ cleaning ability of a chelating agent is almost certainly controlled by the solubility of the metal chelate within CO₂ (3). Also, it is commonly understood that the solubility of a chemical in SCCO₂ depends on the permittivity, polarisibility and volatility of the species. In addition, Lagalante et al. (7) demonstrated a good correlation between the solubility parameter (so substitution about the periphery of the complex) and the mole fraction solubility of copper(II)/ β -diketonates in supercritical CO₂.

Therefore, the better cleaning ability of the β -diketones with methyl substitution or fluorine substitution (hfac) compared to non-substituted ones (cf. Figure 3) can be explained by their better solubility in SCCO₂, as a result of the lower permittivity (methyl substitution) and lower polarisibility (fluorine substitution) of the two respectively.

Metal and oxidized copper selectivity

According to Sievers et al. and Xie et al., during copper metal attack by hfac, copper is firstly oxidized before being chelated (a). This oxidation can be performed by water molecules which are already in the cleaning blend or produced by the reaction between hfac and Cu^(II)O (b).

$$2 C_{5}O_{2}H_{2}F_{6}(H_{2}O)_{2} + Cu^{(0)} \rightarrow Cu(C_{5}O_{2}HF_{6})_{2} + 2 H_{2}O + H_{2}$$
(a)

$$2 C_{5}O_{2}H_{2}F_{6} + CuO \rightarrow Cu(C_{5}O_{2}HF_{6})_{2} + H_{2}O$$
(b)

If this conclusion is generalized to other β -diketones, it is possible that a small water quantity present in CO₂ and/or in additives is able to hydrate a part of the chelating agent molecules. Thus, during the cleaning there is a sufficient amount of each ratio of chelating agent "states" (hydrated and not hydrated) to attack Cu⁽⁰⁾, Cu⁽¹⁾ and Cu⁽¹¹⁾. Indeed, XPS analyses (cf. Figure 6) highlighted that a CO₂/hfac/éthanol mixture was not selective between copper metal and oxidized copper, as a result the process conditions must be fully optimized so as to avoid attack of the copper lines.



Figure 6: XPS spectra before (a) and after a CO₂/hfac/éthanol cleaning (b).

POST ETCH RESIDUES REMOVAL

The cleaning performance of SC CO_2 /additives was also studied for removing copper PER formed during the etching of the stop layer. The objective of this study was to achieve the complete removal of copper PER without extensive attack of the metal features and damage of the material stack. Indeed, an undercut can be observed at the metal/lowk interface (cf. Figure 7 -e-) confirming the high diffusivity of the SC CO_2 /additives throughout the porous material and the differences in properties between the copper/lowk interface and the rest of the copper bulk device. So, an important challenge of this new cleaning is the selectivity of the process between metallic copper of lines and oxidized copper in both polymer residues and copper line surfaces.

The cleaning ability and chemical compatibility of the cleaning process blend was assessed through SEM observations. From the many investigations performed, it was noticed that blends such as hfac/ethanol and in general chelating agent/co-solvent mixtures were ineffective in removing the copper PER (cf. Figure 7 -c-). However, it was found that the joint effect of the chelating agent with an acid in the cleaning mixture was beneficial for PER removal (cf. Figure 7 e -).



Figure 7: SEM pictures before cleaning -a-, after a reference wet cleaning -b- and after a SC CO₂ cleaning using hfac/ethanol -c-, acid/ethanol -d-, acid/hfac/ethanol -e

A DOE was performed on the parameters: Pression (P), Temperature (T), Flow of chemical (F) and processing time(t) to optimise the cleaning and material compatibility of the experimental blend: CO2, ethanol, chelating agent A, acid.

The parameters for the process optimisation were set up to T: 40 -70C, P: 100-180 bars, t: 60-300 seconds and F was set up from 5-20 ml/min while the CO2 flow was kept constant at 6 litres/minutes. For each of the 24 process recipes that the DOE program generated, a copper patterned wafer fragment was run and SEMed. Finally, each one of the SEM micrographs were reviewed and classified from the worst to the better taking into account the cleaning and metal corrosion extent in order to run the DOE program.

The choice to replace the HFAC by the product A as the chelating agent with the experimental blend was driven because the compound does not contain any fluoride, it is not volatile, does not smell and it is cost effective compared to HFAC and/or derivatives.

The pareto plot (fig 9) results emphasised that the cleaning of the PER residues is influenced by many different combined multi- effect factors such as (T-F-t). The results highlighted that ,intrinsically, the temperature was statistically influent towards the cleaning performance of the blend under SCCO2. The temperature can change the density of the mixture from multiphasic to supercritic at identical pression for a given blend and in the worst case, the condensated solution could be put into contact with the copper feature leading to the likely corrosion of the metal feature.

The interaction plot provided more information by looking at the interaction between each process conditions and their influence on the PER cleaning performance. The interesting information that can be extracted form the graph are that low pressure seems more favourable as long as the temperature in low with a low flow. Even more interestingly, the interaction plot indicates that the cleaning is very slightly influenced by the time of injection of the blends at
low temperature and pressure. It must be highlighted that those graphs are taking into account the extreme responses for each parameter, explaining the linearity of the responses.



Figure 9: Pareto chart of the standard effect and the interaction plot calculated by the surface regression program provided with the minitab package.

Indeed, results obtained with acid/chelating agent/solvent/CO₂ blends illustrated that it was possible to remove completely the copper PER without attacking the copper and ULK feature (cf. Figure 7 -f-).

CONCLUSION

These results confirmed that supercritical CO₂-based treatment for copper contamination and PER removal is a very promising cleaning technology. Indeed, more than being compatible with most of the IC materials, SC CO₂/additive cleaning can be very efficient (more than 99%) to remove copper residues inside the porous ULK material film. Two classes of chelating agents were found to be very effective towards ULK decontamination and PER cleaning in the presence of acid. However, subsequent work is required to understand the detailed mechanisms involved during the PER cleaning under supercritical conditions and further optimize the formulations for this new cleaning technology with the aim to upgrade it to an industrial scale.

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Electrochemical Society Proceedings Volume 2003-26

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WATER REMOVAL AND REPAIR OF POROUS ULTRA LOW-*k* FILMS USING SUPERCRITICAL CO₂

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Fourier transform infrared (FTIR) spectroscopy was used to investigate the effect of adding cosolvents (aliphatic C1 to C6 alcohols) and Siprecursors hexamethyldisilazane bearing (HMDS) and trimethylchlorosilane (TMCS) to supercritical carbon dioxide (scCO₂) to dry and repair ashed blanket porous ultra low-k (ULK) methyl silsesquioxane (MSQ) films (JSR LKD5109) (k = 2.4). The drying results showed that all of the aliphatic C1-C6 alcohols removed hydrogen-bonded water. The film repair results indicated that HMDS and TMCS reacted with both lone (SiO-H) and H-bonded silanol (SiO-H) groups. The hydrophobicity of the starting surface before ashing was recovered after HMDS and TMCS treatments as confirmed by contact angle measurements (≥84°). Electrical performance was also restored based on dielectric constant values of 2.4 ± 0.1 . HMDS and TMCS treatments are an effective approach to restore the degradation of ULK MSQ films due to plasma ashing.

INTRODUCTION

Low-*k* dielectric films are the performance driver in back end of line integration. These films are needed for device integration to lower power consumption and minimize cross talk between metal lines. Low-*k* materials currently in production for the 90 nm node are either organics or organosilicates with dielectric constants near 2.8. The second generation of these materials containing manufactured pores filled with air will be needed to achieve k values below 2.4 for the 65 nm device generation and beyond. Pores compromise the structural integrity of low-*k* films as well as expose the film's interior to the outside. The open framework creates significant process integration challenges since the pores must be cleaned, free of etching damage, and capped before deposition of the barrier and seed layers. Etching during pattern formation and ashing to remove photoresist damages and chemically modifies low-*k* layers. Cleaning processes for low-*k* layers are needed to remove photoresist, deveil features, eliminate contamination trapped in pores, and remove Cu. Water is introduced into organosilicate low-*k* layers during ashing of photoresist. The water is present in the form of silanol (Si-OH) groups, which raise the k value typically above 3 and must be removed.

Photoresist removal is commonly implemented using either O_2 or H_2/N_2 plasma treatments and cleaning steps to remove residual contaminants (1,2,3). Wet, dry, and supercritical CO_2 (sc CO_2) cleaning sequences are being investigated for backend applications (4,5). Wet cleaning utilizes an organic solvent or inorganic acid combined with modifiers such as surfactants, corrosion inhibitors, and complexation agents. Dry cleaning utilizes an isotropic plasma. These conventional cleaning approaches, however, face problems with dewetting of nonpolar surfaces, highly porous structures, damage by plasmas, and changes in *k* due to absorption of chemicals. Cleans based on sc CO_2 mixed

279

with small amounts of additives (< 7vol%) such as cosolvents and chelators potentially offer a lower cost solution because of the mass transport, density, tunable solvating power, nonaqueous, low surface tension, reusability and low toxicity of scCO₂.

Several approaches have been used to minimize or repair damage to carbon-doped silicon oxide (CDO) low-k films after photoresist ashing, which typically raises the kvalue to the 3.5 range. Wang et al. (6) showed that the dielectric constant of He plasma treated CDO after ashing was the same as the as-deposited film (k=2.7-2.8). Chang et al. (7) implanted MSQ films with boron (150 keV and 5×10^{15} /cm²), which they propose densified the surface without inducing damage since B is a small atom, and showed that the k value of the as-cured film was maintained. Wang et al. (8) showed that arsenic implantation (80 keV and 5×10^{15} /cm²) had a similar effect in protecting the film during O₂ plasma treatment, but in contrast to boron, arsenic ions damaged the film and raised the k value. Mor et al. (9) reported that pure hexamethyldisilazane (HMDS) vapor reacted with silanol (SiO-H) groups in porous organosilicate glass (POSG) films. The HMDS treatment converted hydrophilic SiO-H groups into hydrophobic SiO-Si(CH₃)₃ moieties, which resisted moisture uptake. The dielectric constant decreased from 3.62 to 2.4 when O₂ plasma-damaged POSG underwent HMDS treatment at 80°C for 15 min. Chang et al. (10) found that trimethylchlorosilane (TMCS) treatment of organosilicate glass (OSG) films at 60°C for 15 min reduced moisture uptake and recovered the dielectric constant of the initial as-cured film (k = 2.6). The dielectric constant decreased from 3.2 after O₂ plasma ashing to 2.8 after TMCS vapor treatment. In addition, studies on nanoporous silica xerogels show that silvlation reactions using TMCS (11,12) and HMDS (13) replace surface hydroxyls with methylsilanes. Clark et al. (14) showed that an HMDS vapor process followed by a 400°C anneal restored the k value of porous methyl silsesquioxane (MSQ) films from 3.14 (post etched/ashed) to 2.43.

Densified fluids heated and compressed to near or above their critical temperature and pressure have solvating properties that are comparable to liquids but mass transfer characteristics comparable to gases making them promising candidates for wafer cleaning applications on both the front and back end of line. scCO₂ is being investigated for cleaning porous materials (15), photoresist removal (16), drying to prevent pattern collapse (17), deposition of metal layers (18), etching metals (19,20) and patterning (21). These applications of scCO₂ are under active development in response to needs for materials and reduced-dimension compatible cleans, new patterning approaches, and low chemical-use processes and have recently been reviewed (22). Supercritical fluids may be especially useful for processing porous films since they have no surface tension. Reidy's group has investigated the application of scCO₂ on low-k materials with TMCS and HMDS (15.23,24,25). The goal of this work is to demonstrate viable processes for water removal and film repair of porous MSQ films using scCO₂. We found that all aliphatic alcohols from C1 to C6 removed water. Both isolated and H-bonded silanol groups reacted with HMDS and TMCS addition to scCO₂. The hydrophobicity of the starting surface before ashing was recovered after HMDS and TMCS treatments as confirmed by contact angle measurements, and the dielectric constants were reduced to 2.4 and 2.6, respectively, which are close to the starting surface value before ashing.

Electrochemical Society Proceedings Volume 2003-26

EXPERIMENTAL

Experimental Setup

The experimental scCO₂ system consisted of a stainless steel reactor fed by a liquid CO_2 bottle (Figure 1). The reactor was a cylinder with a diameter of 1 inch and constructed from ¹/₂ inch wall 316 stainless steel. The total volume was approximately 200 cm³. The reactor consisted of two pieces that screwed together and sealed over a 1 inch diameter seat fitted with a ethylene propylene-90 o-ring (Parker 2-210) in the upper piece. The reactor was cooled to $8^{\circ}C$ in an ice bath and charged with liquid CO₂ (>99.99%, Air Liquide Coleman grade) through ¹/₄ inch stainless steel tubing to approximately 60 atm. After charging, the reactor was heated and required approximately 12 min to cross into the supercritical CO_2 region, and another 3 min to reach steady-state at the desired processing temperature and pressure. Processing times include only the time spent at steady-state conditions and do not include the approximately 15 min ramp. The resistively heated jacket and insulation covering the reactor allowed a temperature set point to be reached within \pm 5°C using a thermocouple and controller. Pressure was read with a Bourdon tube to \pm 20 psig (\pm 1.4 atm). The maximum temperature and pressure achieved with this system were 60°C and 340 atm, respectively. All experiments were run as batch processes. Variations in the temperature and pressure at steady state were observed with this system. After processing the reactor pressure was released quickly through a ¹/₄ inch needle valve reaching ambient in less than 1 min. All experiments reported in this study were for one batch run of a process without a pure scCO₂ rinse after processing.



Figure 1: Schematic of the supercritical CO_2 reactor system. After loading, the reactor was chilled to 8°C and fed with liquid CO_2 to approximately 60 atm. The cylinder was valved off and the reactor heated using a heating jacket and set point controller until the desired steady-state conditions were reached. After processing the fluid was exhausted through a needle valve located at the bottom of the reactor.

Materials

P-type (100) orientated silicon wafers with a minimum resistivity of 0.5 ohm cm containing as deposited and O_2 ashed blanket methyl silsesquioxane (MSQ) films (JSR LKD 5109) were supplied by Sematech. The blanket MSQ film was spun on and cured at 450°C then exposed to a biased O_2 plasma at 25°C for 20 seconds. The wafers were cut into 1.5 x 1.5 cm² samples for processing in the scCO₂ reactor. The co-solvents used to investigate drying were methanol (Analytical reagent, Mallinckrodt Baker, Inc.), ethanol (HPLC grade, Sigma-Aldrich Co.), *n*-propanol (99.9%, Sigma-Aldrich Co.), isopropyl alcohol (CMOS grade, Mallinckrodt Baker, Inc.), n-butanol (ACS grade, Fisher Scientific International), isobutanol (Analytical reagent, Mallinckrodt Baker, Inc.), tertbutanol

Electrochemical Society Proceedings Volume 2003-26

(Reagent grade, Spectrum Quality Products, Inc.), n-pentanol (99+%, Sigma-Aldrich Co.), *n*-hexanol (99+%, Sigma-Aldrich Co.). Silicon-bearing precursors used to study the restoration were hexamethyldisilazane (HMDS, 97%, Sigma-Aldrich Co.) and trimethylchlorosilane (TMCS, 99+%, Sigma-Aldrich Co.). All these chemicals were used as received, without further treatment. A plastic syringe (5 ml total volume) was used to introduce co-solvents into the bottom of the reactor. The air in the reactor was not purged before filling with liquid CO_2 in any of the experiments because the liquid would have been lost out the exhaust port.

Methods

Fourier Transform Infrared (FTIR) Spectroscopy Transmission FTIR spectroscopy (Nicolet Nexus 670 using a MCTA detector) was used *ex situ* to monitor chemical changes in the low-*k* films with a resolution of 4 cm⁻¹. Water removal was calculated using integrated FTIR peak areas in the range from 3150 to 3560 cm⁻¹ on samples before and after treatment.

<u>Contact Angle Measurements</u> Hydrophobicity of ULK MSQ films was determined by measuring the contact angle of deionized water (18.2 M Ω ·cm) with a goniometer (Model 100-00, Ramé-Hart Inc.). All measurements were taken at room temperature and under atmospheric conditions.

Electrical Measurements Electrical measurements were taken on metal insulator semiconductor (MIS) capacitors fabricated after processing in scCO₂. Backside oxide on wafer samples was a particular problem and was etched using a 49% HF solution droppered onto the backside surface and rinsed without wetting the front side. Substrate contact (100 nm thick Au) and gate metal (100 nm thick and 0.1 cm diameter Au) were deposited using an electron-beam evaporator (BOC Edwards E-beam Evaporator Auto 306) and annealed at 375°C for 30 min in a N₂ ambient. *C-V* curves were measured at 1 MHz with an AC bias from -30V to +30V using an Agilent 4284A precision LCR meter at ambient conditions. Electrical measurements were conducted on both as-received and scCO₂ processed samples. All measurements were carried out in a light tight box using a micromanipulator probe with a vacuum chuck. The capacitance in accumulation was used to determine the ULK MSQ film dielectric constant.

RESULTS AND DISCUSSION

MSQ Film Drying

282

ULK MSQ films were processed in $scCO_2$ containing 5-7% cosolvent by volume at 200-300 atm and 45-55°C for a 2 min soak time. The aliphatic C1-C6 alcohols were used as cosolvents. Figure 2 shows the FTIR pre-process, post-process, and difference (post minus pre) spectra for 7% n-propanol added to $scCO_2$ at 280 atm and 53°C for a 2 min soak time. The vibrational stretches of interest are identified as follows (26,27): isolated/geminal O-H stretch (3740 cm⁻¹), hydrogen-bonded O-H groups (3150 to 3600 cm⁻¹), asymmetric CH₃ stretch (2977 cm⁻¹) and symmetric CH₃ stretch (2922 cm⁻¹), and the primary lattice vibrations Si-CH₃ (1277 cm⁻¹, 839 cm⁻¹), Si-OH (942 cm⁻¹), Si-O-Si cage (1134 cm⁻¹), Si-O-Si network (1062 cm⁻¹). The results show that H-bonded silanol (SiO-H) groups were removed from the film without leaving any residue of the cosolvent. Isolated SiO-H groups were created showing that dehydration is a condensation reaction with more than one SiO-H participating. The Si-O-Si bonds of the lattice were relaxed as

shown by the slight shift of the peak at 1062 cm^{-1} to higher wavenumber. The water removal percentage was 30%. Similar results were obtained with the other cosolvents studied. What is not clear from the 5-7% cosolvent addition FTIR results is how the cosolvent is functioning to remove water. One possibility is increasing the solubility of water in the supercritical fluid, since the cosolvents have a higher solubility than water in scCO₂ (28,29). Another possibility is catalyzing the dehydration reaction, which occurs at a relatively low temperature 45-55°C.



Figure 2: FTIR spectra of porous ultra low-k MSQ for 7% n-propanol addition to supercritical CO₂. (a) FTIR spectrum of as received ashed MSQ; (b) FTIR spectrum after exposing sample in (a) to a 15 min ramp to steady-state conditions and a 2 min soak in $scCO_2/7\%$ n-propanol at 280 atm and 53°C; (c) Difference spectrum (b) – (a) (right axis).

MSQ Film Repair

One approach to film repair is to chemically react the hydroxyl groups present in CDO films after etching and ashing with a precursor molecule bearing both a Si atom and a halogen atom. The halogen reacts with the H of the hydroxyl and desorbs leaving the Si part of the precursor and any constituents it contains attached to the film. This reaction is shown schematically as follows

 \sim Si-O-Si-O-H + SiR_nX_{4-n} = \sim Si-O-Si-O-SiR_n + HX

for n = 3 where R is typically an organic group and X is a halogen. The model Si-halogen bearing precursor chosen for study was TMCS [$(CH_3)_3SiCl$]. Another approach is to use a molecule with a weak bond to Si. The model compound using this approach is HMDS [$(CH_3)_3SiNSi(CH_3)_3$], which contains a relatively weak Si-N-Si linkage. Figures 3 and 4 show transmission FTIR pre-, post-, and difference spectra for 1% HMDS addition to scCO₂ at 216 atm and 56°C and 1% TMCS addition to scCO₂ at 215 atm and 58°C, respectively. The FTIR difference spectra show that HMDS and TMCS react with both H-bonded O-H groups (decrease in the O-H peak at 3150-3600 cm⁻¹) as well as isolated O-H groups (decrease in the O-H peak at 3740 cm⁻¹). There is a concomitant increase in the C-H stretch of CH₃ at 2977 cm⁻¹ and 2922 cm⁻¹ and Si-CH₃ peaks at 1277 cm⁻¹ and

283

839 cm⁻¹. The results indicate that the precursors reacted with the silanol groups on the surfaces of the film producing chemical moieties with similar compositions to CDO. On a $Si(CH_3)_3$ moiety basis, more of the TMCS reacted with the film than HMDS.



Figure 3: Repair of ashed porous ultra low-k MSQ film by addition of 1% HMDS to supercritical CO₂. (a) FTIR spectrum of as received ashed MSQ; (b) FTIR spectrum after exposing sample in (a) to a 15 min ramp to steady-state conditions and a 2 min scCO₂/1% HMDS process at 216 atm and 56°C; (c) Difference spectrum (b) – (a) (right axis).



Figure 4: Repair of ashed porous ultra low-k MSQ film by addition of 1% TMCS to supercritical CO₂. (a) FTIR spectrum of as received ashed MSQ; (b) FTIR spectrum after exposing sample in (a) to a 15 min ramp to steady-state conditions and a 2 min scCO₂/1% TMCS process at 215 atm and 58°C; (c) Difference spectrum (b) – (a) (right axis).

284

Contact Angle Measurements

Contact angle measurements as a function of the process applied to MSQ samples are summarized in Figure 5. The left vertical axis gives the contact angle in degrees, and the right vertical axis shows the water removal percentage obtained from referenced FTIR difference spectra using the data in Figures 2-4. The contact angle for an unprocessed blanket film was 106° indicating that the surface was hydrophobic. A rule of thumb is that hydrophobic surfaces have contact angles over 90° and hydrophilic surfaces have contact angles less than 30°. After O₂ plasma ashing, the contact angle was less than 10°, showing that the top surface of the film was strongly hydrophilic. The reason is that O₂ plasma ashing oxidizes Si-CH₃ groups to SiO-H groups (8). After scCO₂ alone and npropanol addition to scCO₂, the contact angles were 14° and 18°, respectively. Both of these surfaces were hydrophilic even though water was removed from these films. These processes left isolated silanol groups on the surface, however, which kept the surfaces hydrophilic. In contrast, HMDS and TMCS addition to scCO₂ produced contact angles of 84° and 87°, respectively, which indicate combination surfaces containing a majority of hydrophobic regions with some hydrophilic regions. In addition to the higher water removal percentage for the Si chemistries, these molecules reacted with both H-bonded and isolated silanol groups on the surface. The reaction and functionalization add chemical groups to the film, which are hydrophobic and could prevent water readsorption from the ambient. The results for pure scCO₂ and with alcohol addition can also be interpreted as showing that moisture readsorbs on these films after processing rehydrating the surface. An open question is whether the Si chemistries seal the pores of the MSQ film. Work to characterize the size of the pores and cap them is ongoing.



Figure 5: Contact angle measurements for unprocessed blanket and ashed ultra low-k MSQ films, and ashed MSQ films processed using $scCO_2$ only, 7% *n*-propanol/scCO₂, 1% HMDS/scCO₂, and 1% TMCS/scCO₂. Left vertical axis shows the contact angle in degrees and the right vertical axis shows the water removal percentage obtained from FTIR difference spectra.

Electrochemical Society Proceedings Volume 2003-26

Electric Measurements

To further investigate film restoration, electrical measurements were made on MIS structures fabricated after processing. Electrical *C-V* measurements were made under ambient conditions in the absence of room light using an Agilent 4284A precision LCR meter. Figure 6 shows dielectric constant values obtained from the capacitance in accumulation for unprocessed blanket MSQ and ashed MSQ, and ashed MSQ samples processed with 1% HMDS added to $scCO_2$ and with 1% TMCS added to $scCO_2$. The unprocessed samples include repetitions. For unprocessed blanket MSQ, the dielectric constant was 2.4 ± 0.1 . This value is higher than expected and may be the result of incomplete removal of the backside silicon dioxide from the wafer samples and inaccuracies in the device area. For unprocessed ashed MSQ, the dielectric constant was 3.5 ± 0.1 , showing that silanol groups increased the dielectric constant to 2.4, and the 1% TMCS/scCO₂ treatment reduced the dielectric constant to 2.6. These results are similar to those reported by Clark using a vapor HMDS process and 400°C anneal (14).



Figure 6: Dielectric constant measurements for unprocessed blanket and ashed MSQ films, and ashed MSQ films processed with HMDS/scCO₂ and TMCS/scCO₂. Left vertical axis shows the dielectric constant obtained from CV plots using the capacitance in accumulation and the right vertical axis shows the water removal percentage obtained from FTIR.

CONCLUSIONS

The aliphatic C1-C6 alcohols studied removed water from ashed blanket MSQ films containing pores, but left isolated silanol groups on the surface of the film. These groups kept the surface in a hydrophilic state. In contrast, HMDS and TMCS dissolved in $scCO_2$ reacted with both isolated and H-bonded silanol groups producing nearly

Electrochemical Society Proceedings Volume 2003-26

hydrophobic surfaces, which prevented moisture uptake. A dielectric constant of 2.4, which was characteristic of non-ashed blanket MSQ, could be recovered using these chemistries. The results suggest that Si bearing precursors are an effective approach to film repair and may be useful in capping pores of ultra low-k dielectrics anticipated to be in production by the 65 nm technology node.

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CLEANING OF FRAGILE FINE STRUCTURES WITH CRYOGENIC NITROGEN AEROSOLS

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ABSTRACT

We have investigated the cleaning of high aspect-ratio and fine structures with cryogenic aerosols. Cryogenic aerosol-based cleaning to employ nitrogen as a source of the aerosols has successfully removed silicon nitride particles on the high aspect-ratio and fine cantilever structures by optimizing the nozzle pressure. This cleaning technique can be applied to fragile fine structures, such as cantilevers and beams both in stencil masks for electron beam lithography and in mobile components for MEMS devices.

INTRODUCTION

As semiconductor device architectures continue to shrink, small-feature/high-aspect ratio structures have become common in the devices. These structures are formed in close proximity to each other and can become stuck together due to the high surface tension of water in the cleaning solution during the wetting and subsequent drying of the structures in an aqueous cleaning. Therefore, dry cleaning techniques that avoid this problem are required.

Cryogenic aerosol-based wafer cleaning is one of the most promising dry cleaning techniques that can remove particles and process residues from silicon wafers without wet chemical solutions [1,2]. In the aerosol cleaning, conventionally used argon aerosols, however can cause the destruction of fragile fine structures, such as cantilevers and beams both in stencil masks for electron beam lithography and in mobile components for MEMS devices.

In this paper, we have demonstrated the cleaning of high aspect-ratio fragile fine structures without their destruction by employing nitrogen as a source of aerosols, whose force of impact against the structures is smaller than argon due to its smaller molecular weight.

EXPERIMENTAL

The cryogenic aerosol-based cleaning system used in this study was developed by Sumitomo Heavy Industries, Ltd. under the license of Air Products and Chemicals

Electrochemical Society Proceedings Volume 2003-26

Incorporated [1]. The schematic diagram of the system is illustrated in Fig. 1. Gaseous nitrogen or the mixture of argon and nitrogen preliminary pressurized and cooled by cryogenic refrigerators was injected into the vacuum chamber through an aerosol nozzle system to generate the nitrogen or the argon aerosol clusters. The nozzle pressure is varied up to 800 kPa. The cryogenic refrigerators allow a large amount of the gas subsequent to the increased gas pressure to be cooled. The aerosol clusters can be accelerated by nitrogen gas jets injected into the chamber from an accelerator nozzle placed adjacent to the aerosol nozzle through mass flow controller at rates up to 20 standard liter per minute (SLM). The pressure of the vacuum chamber is controlled in the range of 4kPa to 8kPa.



Fig. 1 Schematic diagram of cryogenic aerosol cleaning system.

200mm diam. silicon wafers contaminated with silicon nitride particulate matters after their treatment with dilute hydrofluoric acid (dHF) were used to evaluate the particle removal efficiency. The particles whose size is more than 0.13 micron on the surface of the wafers were counted by a surface defect inspection system using laser scattering before and after processing the silicon wafers to determine the particle removal efficiency.

The cantilevers made of 300nm-thick silicon nitride on silicon wafers were used for the evaluation of the pattern destruction due to the impacting aerosols. Their aspect ratio (length/width) was varied from 10 up to 200 and the width was from 80 nm to 100 nm. Figure 2 shows the plan view SEM image of the cantilevers used for the evaluation of the pattern destruction. After processing, the samples were inspected by SEM in terms of their sticktion and destruction, as shown in Fig. 3.

Cleaning experiments were performed at various flow rates of nitrogen for the aerosol acceleration and at various nozzle pressures for the expansion of cryogenic nitrogen or argon. Both the particle-deposited wafers and the cantilever structures were processed with each condition.



Fig. 2 SEM image of the cantilevers with different aspect ratios and widths used in this study.



Fig. 3 (a) (b) (b) destroyed after processing.

RESULTS

Figure 4 shows the particle removal efficiency for argon or nitrogen aerosols as a function of the flow rate of accelerating nitrogen at the nozzle pressure of 400 kPa. The particle removal efficiency increases with an increase in the flow rate of accelerating nitrogen both for argon and nitrogen aerosols. The particle removal efficiency for nitrogen aerosols without acceleration of the aerosols is much lower than that for argon aerosols. The particle removal efficiency aerosols at the flow rate of 20 SLM reaches as high as 98%.

Figure 5 shows that the maximum aspect ratio of cantilevers sustainable in the processing with argon aerosols at the nozzle pressure of 400 kPa as a function of the flow rate of accelerating nitrogen. The 100nm-wide cantilevers whose aspect ratio is even as high as 200 are sustainable in the processing without acceleration of the aerosols, while the 100nm-wide cantilevers whose aspect ratio is more than 5 are destroyed at the flow rate of 20 SLM. The 80nm-wide cantilevers whose aspect ratio is more than 5 are destroyed even without acceleration of the aerosols.

Figure 6 shows that the maximum aspect ratio of cantilevers sustainable after

Electrochemical Society Proceedings Volume 2003-26

processing with nitrogen aerosols as a function of the flow rate of accelerating nitrogen at the nozzle pressure of 400 kPa. The 80nm-wide cantilevers whose aspect ratio is even as high as 200 are sustainable in the processing without acceleration of the aerosols, while the 80nm-wide cantilevers whose aspect ratio is more than 10 are destroyed at the flow rate of 20 SLM where the high particle removal efficiency are obtained.



Fig. 4 Particle Removal Efficiency vs. Acceleration Gas Flow Rate for Nitrogen and Argon Aerosol Cleaning at Nozzle Pressure of 400kPa.



Fig. 5 Maximum Aspect Ratio of Sustainable Cantilevers vs. Acceleration Gas Flow Rate in Argon Aerosol Cleaning at Nozzle Pressure of 400kPa.



Fig. 6 Maximum Aspect Ratio of Sustainable Cantilevers vs. Acceleration Gas Flow Rate at Nozzle Pressure of 400kPa in Nitrogen Aerosol Cleaning.

Electrochemical Society Proceedings Volume 2003-26

It should be noted that there is no optimized flow rate of accelerating nitrogen which satisfies both the high particle removal efficiency and the prevention of cantilever destruction at the nozzle pressure of 400 kPa.

Figure 8 shows that the maximum aspect ratio of cantilevers sustainable after processing with nitrogen aerosols as a function of the nozzle pressure at the flow rate of accelerating nitrogen of 20 SLM. Cantilevers whose aspect ratio is even as high as 200 are sustainable in the processing at the nozzle pressure of more than 600 kPa, regardless of the width of the cantilevers. In contrast, cantilevers whose aspect ratio is more than 20 are destroyed at any nozzle pressure in the processing with argon aerosols at the flow rate of accelerating nitrogen of 20 SLM, regardless of the width of the cantilevers, as shown in Fig. 7.

Figure 9 shows the particle removal efficiency for argon or nitrogen aerosols as a function of nozzle pressure at the flow rate of accelerating nitrogen of 20 SLM. The particle removal efficiency both for nitrogen and argon aerosols reaches as high as 98%, regardless of the nozzle pressure.

It has been found that nitrogen aerosols produced at the nozzle pressure of 600 kPa or higher gave excellent particle removal efficiency without destruction of the cantilevers whose aspect-ratio is as high as 200.



Fig. 7 Maximum Aspect Ratio of Sustainable Cantilevers vs. Nozzle Pressure at Acceleration Gas Flow Rate of 20 SLM in Argon Aerosol Cleaning.



Fig. 8 Maximum Aspect Ratio of Sustainable Cantilevers vs. Nozzle Pressure at Acceleration Gas Flow Rate of 20 SLM in Nitrogen Aerosol Cleaning.

Electrochemical Society Proceedings Volume 2003-26



Fig. 9 Particle Removal Efficiency vs. Nozzle Pressure for Nitrogen and Argon Aerosol Cleaning at Acceleration Gas Flow Rate of 20 SLM.

DISCUSSION

It is generally known that the force of impacting aerosols against the surface results in the removal of particulate matters on the surface if the force of impacting aerosols overcomes the force of adhesion binding the particles to the surface. The same force also causes the destruction of the high aspect ratio and fine structures.

The force of impacting aerosols depends on the size, velocity, density, and hardness of aerosols. Therefore, the aerosols must be smaller, slower, low density, and softer in order to prevent the destruction of the high aspect ratio and fine structures. However, such aerosols are not effective to remove particulate matters. Thus, the size, velocity, density, and hardness of aerosols must be optimized to remove particles on the high aspect ratio and fine structures without their destruction.

It is known that higher nozzle pressure generally provides smaller sized and higher velocity aerosols [3]. The aerosol size will more significantly have an influence on the force of the impacting aerosols than the aerosol velocity at the nozzle pressure of 600 kPa or higher in our experiments. The resultant smaller force of the impacting nitrogen aerosols are considered to cause the prevention of the destruction of cantilevers. On the other hand, the size of argon aerosols is considered to be larger than that of nitrogen at the same nozzle pressure. The resultant larger force of impacting argon aerosols will be the reason why the argon aerosols cannot avoid the destruction of fragile fine structures even at high nozzle pressure.

Our experiments showed that the sufficiently accelerated nitrogen aerosols were able to remove particles even though the force of the impacting nitrogen aerosols is small due to the smaller size of aerosols. Possible mechanisms of particle removal for cryogenic nitrogen aerosols are considered using simulation based on the molecular dynamics.

Figure 10 shows the stroboscopic images of a cryogenic nitrogen aerosol cluster impacting on the particle-deposited surface in the velocities of a) 125 m/s, under Vc and b) 350 m/s, over Vc, where Vc is the critical velocity at which the nitrogen aerosol cluster can take a phase transition to a supercritical state at the impact. The size of the aerosol cluster above the wafer surface is 3 nm in diameter, limited by computer power.

Small carbon particles, whose molecular weight is small to simplify the simulation, are adhered on the wafer surface with the van der Waals force before processing, as shown on the left in Fig. 10 (a) and (b).

Electrochemical Society Proceedings Volume 2003-26

a) Cluster Velocity 125 m/s



Fig. 10 Molecular Dynamics Simulation Result of Nitrogen Aerosol Cluster Impact. Small cubes on the bottom represent carbon particles adhered on the silicon wafer.

The aerosol cluster impacts on the surface, transforming to supercritical fluid, as shown on the middle of Fig. 10 (b). Then, the resultant supercritical nitrogen fluid produces the drag force on the surface by its expansion to efficiently detach the particles from the surface without instantaneous evaporation, as shown on the right in Fig. 10 (b). It should be noted that even smaller size of aerosols as small as 3 nm in diameter has an ability to effectively remove particles on the surface. Once the particles are detached, they are carried away by the gas flow. In the case of the lower velocity impact, the impacting aerosol cluster on the surface instantaneously evaporates without producing the drag force, as shown on the right in Fig. 10 (a). Our calculation based on molecular dynamics shows that the phase transition to supercritical state takes place at the impacting velocity Vc of 150 m/s for nitrogen and 350 m/s for argon. The velocity of nitrogen aerosol clusters with the acceleration gas flow of 20 SLM in the present experiment is high enough to transform to a supercritical fluid, while the size of nitrogen aerosol clusters is smaller than that of argon at the same nozzle pressure. Hence, the nitrogen aerosols can remove particles though the force of the impacting nitrogen aerosols is small.

Electrochemical Society Proceedings Volume 2003-26

SUMMARY

Cryogenic aerosol cleaning to employ nitrogen as a source of the aerosols has successfully removed particles on the fragile fine structures by optimizing the nozzle pressure. Our simulation based on molecular dynamics shows that the pressure and temperature of impacting nitrogen aerosols against the surface reach the critical point of nitrogen. Hence, resultant supercritical nitrogen fluid will be considered to generate relatively large shear force to remove particles on silicon wafers even when the force of the impacting nitrogen aerosols is small.

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Post- CMP Cleaning

Electrochemical Society Proceedings Volume 2003-26

ADVANCED FRONT END OF THE LINE CLEAN FOR POST CMP PROCESSES

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ABSTRACT

As devices continue to shrink below 100 nm, wafer surface preparation has become more critical to high yield devices [1]. Numerous techniques have established a post CMP cleaning procedure that focused mainly on reducing the defects (particles) on the wafer surface. Most of the process of record (POR) methods typically use brush scrubbers and are based on an RCA type process [2]. These procedures have proven to be costly and do not necessarily produce the desired wafer surface characteristics. In this paper, we propose an advanced front end of line (AFEOL) clean as an alternative to high cost scrubbing wafer-cleaning systems. The results show that the AFEOL process is a viable clean that meets the tight manufacturing low particle requirements.

INTRODUCTION

The manufacturing of advanced integrated circuits (IC) typically uses about 350 steps. One fourth of these steps are dedicated to wafer surface cleaning to remove any contaminants from the previous steps and/or prepare the surface for the subsequent steps. During IC manufacturing, it is difficult or sometimes impossible to measure every production wafer. Instead, monitor wafers are processed at the same time along with the product wafers. These monitor wafers (sometimes called witness, filler, or dummy) provide information on how the batch was processed. If the monitor wafers show good results, then the production wafers are assumed to be good as well. To maximize cost savings these monitor wafers are reclaimed. At the end of the IC manufacturing cycle, these wafers are reconditioned and used again for a new cycle. That's one of the reasons that wafer surface preparation of these reclaimed wafers has become one of the most critical steps in the manufacturing of semiconductors. With requirements to make sub 100 nm devices and the economic and environmental pressures, it has become clearer that new cleaning techniques must be developed. Numerous techniques have established a post CMP cleaning procedure that focused mainly in reducing the defects (particles) on the wafer surface. The wet cleaning methods include immersion cleaning (chemical and rinsing action aided by megasonics), spray cleaning, and contact cleaning [3]. Most of the process of record (POR) methods typically use brush scrubbers and are based on an RCA type process [2]. These procedures have proven to be costly and do not necessarily produce the desired wafer surface characteristics e.g. low particles counts, undetectable metals, limited surface roughness, and undetectable organics. New techniques must be cost sensitive and provide the lowest cost of ownership [4]. This includes a smaller tool

299

footprint, lowest chemical consumptions, and that exhibits no environmental, safety and health concerns. This paper compares results obtained from an advanced front end of line clean versus POR cleans for both particle counts and metals. The data show that the AFEOL cleaning approach is a viable one that meets the more stringent semiconductors manufacturing requirements.

EXPERIMENTAL PROCEDURE

Wafers, highly contaminated from CMP processing, were processed in an AFEOL fully automated GAMA system. In initial attempts to clean these types of wafers, the standard recipe was tested. The standard recipe recommended by Akrion for Front End of the Line wafers is the AFEOL process (shown below):

Table 1. Standard AFEOL clean sequence			
Step/Concentration	Time, min.	Temp., C	Purpose
DIO3	5	24	Remove Organics
SC1 (1:2:30) w Megasonic	6.5	60	Remove Particles
QDR Rinse	7.5	Amb. ~ 20	Rinse off chemicals
HF/HCI (1:2:200)	5	24	Remove Metals
Ozone HFC Rinse	8	Amb. ~ 20	Regrow Oxide
LuCID Dryer	10	Amb.	Dry wafers

Table 1: Standard AFEOL clean sequence

This recipe was taken as a starting point to give an indication of the type of cleaning needed for these wafers. However, due to the amount of contamination on the wafers (2000 – 16000 LPD's @ 0.16 μ m) it was clear that more aggressive cleaning was required. Various parameters in the above recipe (time, temperature, concentration) were adjusted to ascertain if they would result in sufficient cleaning but each time the results were unsatisfactory as detailed in the discussion section.

RESULTS AND DISCUSSION

Figure 1 shows typical contamination levels on the test wafers. Fig. 2 and 3 show the high particle removal efficiency (as measured by the slope of the regression line) of the system at both low and high contamination levels. However, the final counts obtained from the standard AFEOL cleans were still higher than the desired values as shown in Fig. 4. Using design of experiments techniques, a more process optimization was required. Increasing the SC1 time and temperatures yielded better results but was found to be not economically feasible approaches.

Electrochemical Society Proceedings Volume 2003-26



Further testing lead to the replacement of the initial DIO3 step with an HF step. This step was designed to remove the native oxide (dirty) by HF and thus enable the cleaning chemistry to remove remaining particles. The results of that change were significantly better as shown in Fig. 5. Further adjustments of the remaining parameters were necessary until the goal of clean wafers had been reached. The final breakthrough was the addition of a megasonic into the post SC1 rinse tank. The final recipe was briefly as follows and detailed below in Table 2: (HF+HCI)/Rinse/SC1/Rinse/(HF+HCI)/Rinse/Dry. As shown in Fig. 6, the final counts on the wafers were less than 20 particles at 0.16 μ m for all wafers tested.

See Table 3 below for a summary of results associated with each clean. As seen in Table 3, particle counts on the wafer were lower than those obtained for the POR. In addition, the standard deviation for these results was much tighter than that of the POR, which means the resultant AFEOL clean is more robust. No metals were detected above 5E9 atoms/cm² on the wafer surface when the modified AFEOL was used.

Step/Concentration	Time, min.	Temp., C	Purpose
HE/HCI (1:2:200)	5	24	Remove metals and contaminated oxide
	Ŭ	27	Rinse off chemicals
HFC Rinse –			(and passivate wafer
w/ or w/o Ozone	8	Amb. ~20	surface)
SC1 (1:2:30) w/ Megasonic	10	70	Remove particles
QDR Rinse w/ Megasonic	10	Hot	Rinse off chemicals
	5	24	Remove chemical oxide and
TIP/TICI (1.2.200)	5	24	Dingo off chomicals
			(and passivate wafer
Ozone Rinse	8	Amb. ~ 20	surface)
LuCID Dryer	10		Dry wafers

Table 2: Modified AFEOL clean to include HF/HCI to remove contaminated oxide followed by ozonated rinse.

Table 3: Summary of Final Particle Counts after Various Cleaning Methods.

Run	Process	Pre	Post
		@ 0.16um	@0.16um
A	POR	2000-10000	40-100
в	AFEOL	2000-10000	90 - 260
С	AFEOL x 2	2000-10000	30 - 120
D	AFEOL (SC1 10mins @ 70degC)	2000-10000	10 - 350
E	AFEOL + 2nd SC1	2000-10000	10 - 240
F	DIO3/SC1/Rinse/Dry - No HF	2000-10000	30 - 470
G	HF/HCI-O3Rinse-SC1-Rinse-HF/HCI- O3Rinse-Dry	2000-10000	20 - 100
Н	HF/HCI-Rinse (No O3)-SC1-Rinse w Meg-HF/HCI-O3Rinse-Dry	2000-10000	4 - 50
1	HF-(Rinse+O3)-SC1 15mins-Cold Rinse w Meg-HF/HCI-O3Rinse-Dry	2000-10000	< 20

As stated earlier, the processes were designed for the test grade polished wafers. When these recipes implemented to process wafers in manufacturing, it has become apparent that the wafer quality can negatively affect the results. This can be easily seen when the wafers are examined at a higher resolutions e.g. $0.12 \,\mu m$ or lower as measured on KLA_Tencor SP1^{TB1} laser scanner. As shown in Fig. 6, the wafer exhibits a circular pattern of particles clustered in the center. When these wafers were processed in the designed SC1, an increase in the number of light point defects (LPDs) was repeatedly experienced. For example, the LPDs counts increased from 267 to 377 as shown in Figure 7 or from 215 to 975 as shown in Fig. 8. These defects are theorized to be crystal-originated pits or

302

particles (COPs) and cannot be removed by the cleaning process. The number of defects was found to increase with the SC1 concentration, time and temperature. The H_2O_2 concentration has become very critical to minimize these defects. The higher the H_2O_2 concentration the lower the number of pits induced.



Another phenomenon was discovered when examining these wafers at these low particle sizes when processed in HF followed by an SC1. Hydrophobic wafers are very sensitive the SC1 and ionic impurity contents. Metal-induced pitting was reported by Knotter [5] and was confirmed in these results as can be seen in Fig. 8. This pattern of defects was shown to be permanent in nature and cannot be removed by any cleaning process including scrubbing. This defect was also found to increase with the SC1 concentration, time, temperature and metal impurity levels. The process was further optimized to include a passivation step using ozonated rinse after HF [4,6]. An oxide film thickness of about 10 A was found to be sufficient to protect the Si from the metal-induced pitting in the SC1. Once wafers were passivated, no microroughness was found on any of the wafers tested as shown for example in Fig. 9. An average of particle final counts on the wafers of less than 20 at 0.12 μ m was reported following the optimized recipes and using pits-free wafers.



Fig. 9: Final counts on wafers clean in the optimized newly developed AFEOL clean (0.12 $\mu\text{m})$

CONCLUSIONS

A test study was conducted to compare an existing (POR) process with a new process (AFEOL) for post CMP cleans. The results show that the AFEOL clean outperformed the POR. The technique was slightly modified to meet the tight manufacturing requirements. The addition of the dHF or dHF/dHCl was necessary to remove the native oxide and contaminants in it and thus enabling cleaning. The results also show that the use of the megasonic energy and hot rinse added additional robustness and statistically tight counts on the wafers surface. The use of ozonated rinse after HF was found to be critical to prevent the metal-induced pitting on hydrophobic wafers from the SC1. The final particle counts and elemental metal signature were far lower than those obtained in the POR cleans. The study shows clearly that the surface physics of these reclaimed wafers must be understood in order to obtain meaningful data.

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LOW CARBON CONTAMINATION AND WATER MARK FREE POST-CMP CLEANING OF HYDROPHOBIC OSG DIELECTRICS

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ABSTRACT

Organosilicate glasses (OSG) are the low-k dielectric of choice for the 90nm technology node and beyond. Various OSG dielectrics are commercially available, such as Black Diamond, Coral, Orion, Aurora, etc. The high methyl content of OSG yields a hydrophobic surface, leading to a challenge of wetting surfaces when cleaning them with aqueous solutions after a chemical-mechanical-planarization (CMP) process. Introduction of surfactants has resulted in challenges to remove them. Several post-CMP cleaning issues have complicated integration of OSG dielectrics; carbon residues and water marks. Benzotriazole (BTA) is commonly used to passivate copper films and is a component in most copper Step 1 CMP slurries. BTA has been identified as a source of organic contaminates and is often difficult to remove from copper patterns. Water marks can mask killer defects by saturating inspection tools. This paper will assess the ability of several post-CMP cleaners to remove BTA and also eliminate water marks.

INTRODUCTION

Carbon residues on the dielectric can result in poor adhesion of subsequent process films, resulting in pull-outs during polishing, voids during plating, and delamination of buried films after elevated thermal cycles, due to decomposition of the organic contaminate. Quench or staging solutions for polished copper wafers typically contain triazoles to provide corrosion protection for the copper pattern. Copper slurries also contain triazoles and other organic components to form a passivation layer to control the chemical planarization process. The copper oxidation process involves sequential oxidation of Cu and cuprous oxide (Cu₂O) to cupric oxide (CuO). The most commonly used copper corrosion inhibitor is benzotriazole (BTA) which interacts preferentially with Cu₂O. The triazoles and BTA in particular, have been identified as a source of organic contaminates during the cleaning process. Other sources of organic contaminates include pad shedding, tool materials of construction, o-rings and seals, wafer boats, brushes, etc. BTA appears to be a common organic contaminate source.

During the copper CMP process, the wafers are often protected during staging for the next process step by spraying a dilute aqueous solution of BTA on the wafers and keeping them wet. After the CMP process, the wafers are often immersed in a dilute

Electrochemical Society Proceedings Volume 2003-26

aqueous BTA solution, rinsed with DI water, and spun dry and then staged for the next process level (i.e., copper seed layer deposition). The use of surfactants can result in copper and dielectric surfaces coated with organic surfactant. Prior to the copper seed layer deposition, the surfactant and/or BTA-Cu complex must be removed to ensure the plating seed layer adheres to the previous copper level. Argon-ion back sputtering, a long used process to remove aluminum oxide from aluminum patterns prior to the next process step, has not been successfully used for copper. Contamination of the plasma tool with organic degradation products has limited throughput significantly. The use of plasma processing, either oxidative or reductive, to remove organic contaminates may be limited by the choice of dielectric. Some low-k dielectrics are more easily damaged by a plasma process to achieve an improved cost of ownership (CoO), appropriate wafer throughput, and no damage to the dielectric. Post-CMP cleaners have been tested which significantly reduced organic contamination from the polishing process (1). Process optimization of both the CMP process (1) and the cleaning tool can reduce organic contamination.

Water marks can saturate metrology tools that measure light point defects (LPD) masking detection of killer defects. The cause of water marks on OSG is not completely understood. Data from front-end-of-line (FEOL) processing of silicon indicates that water marks are caused by etching of the silicon. Silicon and copper are hydrophobic. Silicon dioxide (SiO₂) and copper oxides are hydrophilic. In FEOL silicon cleaning, the water mark could be either the pit remaining where the silicon was etched when the aqueous solution beaded up on the surface, or the insoluble oxidation products deposited on the surface of the silicon. The pH of the cleaner could have an impact on the production of water marks. The generation of water marks on silicon surfaces during rinsing with DI water is a function of pH and the presence of oxygen (2, 3). Reducing the oxygen level in DI water has shown an impact on water mark formation (2). At low pH, H₂SiO₃ (meta silicic acid) has reduced solubility in water and remains on the surface (3). Silicic acid is soluble at higher pH values and does not precipitate on the wafer surface (3). Introduction of a surfactant to reduce surface tension and improve wetting of hydrophobic surfaces may be a solution to eliminate water marks. However, the surfactant, which may not be easily removed, can become a source of organic contaminates. One can also introduce DI water-free drying methods, such as isopropyl alcohol (IPA) vapor drying. Utilizing IPA vapor drying in the post-CMP cleaning process will increase the CoO due to hazardous waste disposal costs for used IPA, increased cleaning tool cost, necessity for fire suppression systems, etc. Designing a cleaner to eliminate water marks on hydrophobic OSG may offer the lowest CoO for the post-CMP process.

EXPERIMENTAL

Blanket copper seed wafers were treated with an aqueous 10ppm BTA solution (pH of 5.3) at room temperature (23°C) as follows; two hour static immersion, 30 second DI water rinse, and an N₂ dry. The copper seed wafers contained 1000Å of PVD copper. The BTA treated wafers were cleaned with various commercially available post-CMP cleaners in a single wafer, spin-spray, non-contact process tool at room temperature as follows; 60 second chemical treatment at 100 rpm, 30 second DI rinse at 100 rpm, and 30 second N₂ dry at 2500 rpm. A Scienta ESCA Model 300, equipped with a monochromatic

306

Al k_{α} x-ray source, was used to acquire XPS spectra. A take off angle of 15° provided a sampling depth of about 25Å. However, at a take off angle of 90°, the sampling depth was about 75Å. The ratio of nitrogen to copper was calculated from the N 1s and Cu 3p XPS spectra and used to estimate the thickness of the deposited BTA film and the percentage of BTA removed with the cleaner. The estimated errors were $\pm 2\%$ for the atomic percentages and ±5% for the N/Cu ratios. Patterned uncapped Coral wafers (Sematech 854) were also examined on an AIT1 and SEM to classify defects.

Unpolished blanket Coral wafers were used for water mark evaluations. An SP1 was used for whole wafer scans to look for the typical radial spin-out pattern of water marks. Contact angles for DI water, pre- and post-cleaning, and for cleaning solutions were measured on a Goniometer using hardware and software from Connelly Applied Research. Dilutions of surface preparation products were verified using a Model 330i WTW Conductivity meter.

RESULTS

BTA and Organic Contaminate Removal Capabilities

Figure 1 contains contact angle measurements for unpolished Coral wafers for DI water, ESC 794, and ESC 797. The ESC products were diluted 20:1 with DI water. The diluted ESC products wet the surface of the hydrophobic OSG significantly better than DI water by itself since the contact angles are about half of that for DI water.



Contact Angle on Unpolished Coral

Figure 1. Contact angle measured on unpolished Coral wafers.

Table 1 contains XPS data for copper and nitrogen obtained from copper seed wafers with various processes. The data includes untreated controls, samples treated with BTA, and samples treated with BTA followed by non-contact cleaning with various cleaners. The different take-off angles were run to estimate the BTA-Cu film thickness. Using a

Electrochemical Society Proceedings Volume 2003-26

take-off angle of 15°, the ratio of nitrogen to copper on the BTA treated sample, was 2.95 \pm 0.15. The number of nitrogen atoms per BTA molecule is three, indicating that the BTA-Cu film was thicker than about 25Å. At a take-off angle of 90°, the ratio of nitrogen to copper for the BTA treated sample was 0.56 \pm 0.03, indicating that the film was less than 75Å thick since a significant copper signal came from the metal below the BTA-Cu film. Several ESC surface preparation products that were tested (e.g., ESC 85A, ESC T794, and ESC 797) achieved complete removal of the BTA-Cu film with a 1 minute, non-contact spin-spray process. One post-CMP cleaner, Product E, left a significant amount of BTA on the copper when used at its normal dilution of 50:1. ESC 784 also did not remove 100% of the BTA when used at a dilution of 30:1 in a non-contact mode. However, using ESC 784 at 30:1 in either a Megasonics bath or with brushes may have resulted in 100% BTA removal efficiency.

Table 1. XPS data and BTA removal efficiency for copper seed wafers after various treatments.

Treatment	XPS Angle (°)	Cu (%)	N (%)	N/Cu	% BTA Removed
Untreated	15	92.8	7.2	0.08	N/A
Untreated	90	98.9	1.1	0.01	N/A
BTA	15	25.3	74.7	2.95	N/A
BTA	90	63.9	36.1	0.56	N/A
BTA→ESC 784 (30:1)	15	90	10	0.11	96
BTA→ESC 797 (30:1)	15	95.7	4.3	0.04	100
BTA→ESC 85A (30:1)	15	94.8	5.2	0.06	100
BTA→ESC T794 (24:1)	15	95.3	4.7	0.05	100
BTA \rightarrow Product E (50:1)	90	85.3	14.7	0.17	67

Data in Figure 2 was generated by Rodel, Inc. using an AIT1 and SEM and indicates the organic contaminate removal capabilities of several ESC surface preparation products at two dilutions. At a dilution of 30:1, ESC 794 and ESC 797 removed all organic defects from the Sematech 854 patterned Coral wafers. ESC 784 was slightly less effective in removing organic defects from the copper patterns, but was still better than that for their previous process of record (POR). At much higher dilutions (e.g., 120:1), ESC 794 was still quite effective in removing organic defects, indicating a very broad dilution latitude.

Copper Passivation

Removing the BTA could result in copper corrosion if the staging time between the CMP process and the next step was over a few hours long. Customers prefer to either leave a monlayer of BTA or replace the BTA film with a pasivation film which is more easily removed. Table 2 contains XPS data for film thickness for several ESC cleaners, two of which contained copper passivators. ESC T794B and ESC T794M contained two different copper passivators and after cleaning patterned 854 wafers, they left a very thin passivating film on the exposed copper. ESC T794M provided a passivating film that was << 25Å thick, approaching a monolayer, compared to a typical BTA film that was <75Å thick.

Electrochemical Society Proceedings Volume 2003-26

Treatment	XPS Angle (°)	Film Thickness (Å)
Untreated	15	0
BTA	15	25 < t < 75
$BTA \rightarrow ESC T794$	15	0
ESC T794B	15	< 25
ESC T794M	15	<< 25

Table 2. Copper passivating film thickness remaining after removing BTA during cleaning.



Figure 2. Organic defect counts versus ESC product and dilution

Water Mark Elimination

Figure 3 shows SP1 whole wafer defect scans for OSG blanket wafers (a) prior to polishing, (b) post-polish and post-clean with Product E, (c) post-polish and post-clean with Product A, and post-polish and clean with ESC 794. The polish and cleaning parameters were the same for all wafers tested. The SP1 data for ESC 794 indicated an order of magnitude lower defect counts, compared to the pre-polish data, and over two orders of magnitude lower defect counts compared to Product E. ESC 794 showed more than an order of magnitude lower defect counts compared to Product A. The SP1 defect map for both Product E and Product A showed a typical radial pattern, indicative of water marks. Several factors contributed to the lower defect counts for ESC 794, which included additives in the product and the detergency of one of the solvents. ESC 794 does not contain a surfactant.

309



a. Before polishing, N=1,100 defects.



b. Post-polish and post-clean for Product E, N=14,657 defects.



c. Post-polish and post clean for Product A, N=5,580 defects



d. Post-polish and post-clean for ESC 794, N=172 defects.

Figure 3. SP1 whole wafer scans for defects $> 0.16\mu$ m for unpolished Coral wafers which were cleaned in a non-contact, spin-spray processor.

CONCLUSIONS

Several surface preparation products have been tested which were capable of removing BTA from the surface of copper in a non-contact cleaning mode. The organic solvents used in the products allow them to remove organic contaminates even at high dilutions with DI water. The efficiency for removing organic contaminates may also be dependent on pH. The same products were also capable of preventing water marks on hydrophobic OSG, possibly due to their wetting capabilities, since their measured contact angles were significantly lower than that for DI water. In addition, one of the products from a competitor which resulted in water marks also did not entirely remove BTA.

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Electrochemical Society Proceedings Volume 2003-26

ADHESION AND REMOVAL OF SILICA AND ALUMINA SLURRY PARTICLES DURING Cu CMP PROCESS

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ABSTRACT

This study aims to investigate the interaction forces between slurry particles and wafer surfaces during the Cu CMP. The interaction forces between slurry particles and Cu surfaces are measured and calculated. The DLVO theory was used to calculate these forces by measuring the zeta potentials of the particles and the surfaces. The interaction force was obtained directly by measuring the force on the particles as a function of the distance between the particle and the surface. Likewise, the magnitude of particle contamination on the wafers was measured by field-emission scanning electron microscope after the wafers were polished. The weakest repulsion force was measured between particles and Cu surface at pH3. Similarly, the highest number of particles was observed on Cu surfaces in the pH3 solution after they were polished.

INTRODUCTION

Due to the low resistivity and high electromigration performance of Cu, it is considered a much better interconnection material than the currently used Al-based alloys [1]. However, while there is a clear advantage in using Cu as an alternative material to Al, there are several challenges that must be overcome. One such challenge is the difficulty involved in the patterning of Cu by dry etching. The damascene technology using chemical mechanical planarization (CMP) is the only technology that can provide global planar surfaces and patterned Cu interconnection with a large process window [2].

The other problem of Cu CMP is Cu contamination during device manufacture. Cu is considered a very serious metallic contaminant for silicon devices. The detrimental effects of Cu contamination of the intermetal and interlevel dielectric are well known [3]. Compared to other materials such as oxide and W, Cu is a softer material and tends to cause more scratches and dishing during CMP. Thus, Cu CMP involves two polishing steps. In the first step, acidic-pH alumina or silica slurry is used for faster removal of Cu until the barrier surface is exposed. In the second step, alkaline silica slurry is commonly used to bring the ratio of the polishing selectivity of Cu to the barrier layer to the dielectric or low dielectric constant materials close to 1:1:1.

After the second polishing step, the Cu, TaN, and dielectric materials are exposed to silica slurry particles. The interaction of particles with these polished surfaces will determine the polishing behavior and the level of particle contamination after Cu CMP.

In this paper, the interaction forces between particles and surfaces during Cu CMP were calculated based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for different pH ranges [4, 5]. The adhesion forces between the particles and surfaces were also experimentally measured using an atomic force microscope (AFM). Likewise, the magnitudes of particle contamination on the Cu surfaces were observed after they were polished to confirm the resulting interaction forces.

Electrochemical Society Proceedings Volume 2003-26
For this experiment, Cu deposited wafers were used as substrates. Cu deposited wafers were pre-cleaned in a DHF solution and then rinsed with DI water to remove organic contaminants.

The zeta potentials of all materials used in this study were measured as a function of pH, using a LEZA-600 (Otsuka Electronics. Co.) zeta potential analyzer.

The interaction force was measured using an AFM (AutoProbe® CP Research, Park Scientific Co.) by analyzing the force on the cantilever as a function of the distance between the cantilever and the surfaces in a 10^{-3} M KCl solution at different pH values. A liquid cell was used. For the interaction force measurements, a glass particle with a radius of 20 μ m (Duke Scientific Co.) was attached to a tipless cantilever of AFM. Figure 1 shows the optical micrograph of a silica particle on a tipless cantilever.

The wafers were polished with colloidal silica slurry on a polisher (PM5 polisher, Logitech Co.). The rotation speeds of the head and platen were set at 30 rpm. The pressure of the carrier was 3 psi, and the polishing time was set at 1 min. The slurry flow rate was 120 ml/min. For the preparation of the slurry, a shaker and ultrasonic power were applied for 60 min. and 30 min., respectively. The slurry for Cu CMP was respectively prepared by mixing 3 wt% alumina particles, 6 wt% colloidal silica particles and a corrosion inhibitor (BTA, 0.03wt%) in a 10⁻³ M KCl solution (the same chemical composition as that of the solution for the AFM measurements). The polished wafer surfaces were observed using Field-Emission Scanning Electron Microscopy (JSM-6330F, JEOL Co.) to measure the level of particle contamination on the surfaces.

RESULTS AND DISCUSSIONS

The zeta potentials of the slurry particles and wafers were measured as shown in Figure. 2 (a), (b) and (c). Colloidal silica particles showed very stable suspension in the pH ranges investigated. Alumina particles have IEP at pH 9.829. Figure 2(c) shows the zetapotential of Cu as a function of solution pH. Due to the high conductivity of the Cu surface, Cu particles instead of Cu wafers were used to measure zeta potential. All surfaces showed negative zeta potentials in the pH range investigated.

The DLVO theory [4,5] estimates the repulsive and attractive forces resulting from the overlap of electric double layers and the London-van der Waals force, as a function of inter-particle distance. The total interaction (V_T) occurring between the particles and the wafer surface in the solution is the sum of van der Waals force (V_A) and the electrostatic force (V_R) , as shown in equation (1) below.

$$V_T = V_A + V_R \tag{1}$$

If a small inter-particle surface separation (H) is assumed, the van der Waals force between a sphere and a substrate can be expressed as

$$V_{A} = -A_{132} \frac{R}{6H^{2}}$$
(2)

where, A_{132} is the Hamaker constant for surfaces 1 and 2 in a dispersion medium 3, calculated based on an A11 value, and R is the radius of a sphere.

The calculation of the electrostatic force is more complex due to the overlapping of the diffused double layers between two surfaces. It must rely on numerical solutions or various approximations. Overbeek's approximation [6]

-9] was used for the calculation of the electrostatic force due to larger than 25mV zeta potentials on surfaces, as shown below:

$$V_{R}(H) = \frac{64\pi \epsilon Rk^{2}T^{2}\gamma_{1}\gamma_{2}}{e^{2}z^{2}} \exp[-\kappa H], \quad \text{where,} \quad \gamma = \frac{\exp[ze\psi_{d}/2kT]-1}{\exp[ze\psi_{d}/2kT]+1}, \quad (4)$$

 ε is the permittivity of the dispersion medium, and k is Boltzmann constant, and and T is the temperature. and z is the counter ion charge number, and R is particle radius and and debye length $1/\kappa$, is $(8\pi nv^2 e^2/\epsilon kT)^{1/2}$, while ψ_d is the zeta potential of surfaces.

Figure 3(a) and (b) shows respectively the DLVO total interaction force between an alumaina, silica particle and wafer surfaces as a function of distance between them. A stronger attractive force was calculated for alumina and silica particles on the Cu surfaces in acidic than in alkaline solutions. Also a stronger attractive force is observed at the alumina particle compared with silica particle at the same pHs. It indicates that alumina particles have more attractive than silica particles on Cu surfaces.

Figure 4(a) and (b) show the measured interaction forces between the alumina, silica particles and Cu surfaces, respectively. A strongest adhesion forces were measured for alumina and silica particles on the Cu surfaces in acidic than in alkaline solutions. These results are relation with zetapotential and well agree with calculated results through the DLVO theory. In all pHs investigated, the measured interaction forces showed the very similar trends as the calculated ones. A stronger adhesion of particles on surfaces was measured in acidic than in alkaline solutions.

In order to confirm calculated and measured interaction forces, the polishing of Cu wafers was performed respectively using the alumina and colloidal silica slurry. After polishing these surfaces, FESEM was used to observe the magnitude of particles left on each surface. Less particles were observed on Cu surface at pH11 (Figure 5(a) and 6(a)). However, the greatest number of particles were observed on Cu surfaces at pH7 and pH3. It could be concluded that Cu surfaces are very susceptible to the particle contamination in acidic slurry during Cu polishing. In all pHs investigated, the inspection of particle contamination showed the very similar trends as measured interaction forces and the calculated ones

SUMMARY

The zeta potentials of slurry particles and Cu surface were measured to calculate the total interaction force between the particles and substrates based on the DLVO theory. More attractive forces were calculated between alumina, colloidal silica particles and Cu surface in acidic rather than in alkaline slurry. The adhesion force between colloidal silica particles on the cantilever and the wafers was measured using an AFM. The alumina and colloidal silica particles showed the strongest adhesion at acidic pH. However, the weakest particle adhesions were observed at the alkaline pH. Experimental measurement of interaction forces supported the theoretical calculation of interaction forces between alumina, colloidal silica particles and Cu surface. In order to compare these results, particles on substrates were observed by FESEM after the surfaces were polished with alumina and colloidal silica based slurries. The smallest and largest number of particles were observed at pH3, and pH11, respectively. The pH of the slurry and the zeta potentials of the surfaces played important roles in controlling the interaction forces of particles and contamination level on the polished surfaces.

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314

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Electrochemical Society Proceedings Volume 2003-26



Figure 1. The optical micrograph of a silica particle on a tipless cantilever



Electrochemical Society Proceedings Volume 2003-26



(c) Figure 2. The zetapotential of (a) colloidal silica particles, (b) alumina particles and (c) Cu as a function of solution pH



Figure 3. DLVO total interaction force between Cu and (a) alumina particles (b) colloidal silica particles in acidic, neutral, and alkaline solutions

Electrochemical Society Proceedings Volume 2003-26





Figure 4. Measured interaction forces between Cu wafer and (a) alumina particle (b) the silica particle in acidic, neutral, and alkaline solutions



Figure 5. FESEM images of particles on Cu wafer after polishing in alumina based slurry of (a) pH 11, (b) pH 7 and (c) pH 3 $\,$

Electrochemical Society Proceedings Volume 2003-26





Electrochemical Society Proceedings Volume 2003-26

POST COPPER CMP CLEANING GALVANIC PHENOMENON INVESTIGATED BY EIS

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In the damascene process, dendritic growth is observed on some parts of the circuit in some conditions during the post-CMP cleaning step. To understand electrochemical mechanism leading to this parasitic phenomenon copper behaviour in oxalic acid media was investigated by cyclic voltammetry and impedance measurement in both cathodic and anodic potential range. Copper-oxalate complexes in the solution are taken into account. The role of diffusion and oxygen is studied.

INTRODUCTION

For its very good electrical conductivity, copper $(1.7 \ \mu\Omega \ cm)$ is growingly replacing aluminum $(3.0 \ \mu\Omega \ cm)$ as the interconnect material for integrated microcircuits. A dual damascene technique must be used to adjust to the impossibility of etching the copper. This method leads to using the CMP process to remove overburden copper and the liner layer over the insulating dielectric material.

In this last stage and more precisely during the post CMP cleaning process which uses acidic solutions, galvanic corrosion can be induced in particular areas. In the microelectronic device, the wet-chemical surface creates a galvanic cell where copper lines on the P region behave as an anode and copper lines on the N⁺ region behave as a cathode (see Figure 1) copper dissolves on the first one and is deposited on the second one. Therefore, in critical and reproducible conditions (presence of light, non respect of design rules...), dendrites can be generated on the cathode and could short two copper lines. Even though this phenomenon is now well known, the electromechanical mechanisms it involves are yet to be investigated.



Figure 1: Scheme showing the possible sources of the dendrite growing problems arising at copper interconnects.

Electrochemical Society Proceedings Volume 2003-26

At first, the complexation of copper cations with oxalate anions was examined. The dissolution and electrocrystallisation of copper in an oxalic aqueous medium were studied by means of EIS (electrochemical impedance spectroscopy). This study was performed in a large domain of acid concentrations (0.1 to 0.00001 M) to determine which conditions can induce the phenomenon: the problem may arise during the step of acid elimination by water.

COMPLEXATION OF COPPER CATIONS WITH OXALATE ANIONS

Oxalate anions, denoted Ox^{2-} for $C_2O_4^{2-}$, are known to form stable complexes with copper. They react with Cu^{2+} cations in aqueous solutions to form two soluble complexes:

$$Cu^{2+} + Ox^{2-} \underbrace{\longrightarrow} Cu(Ox)$$
$$Cu^{2+} + 2Ox^{2-} \underbrace{\longleftarrow} (Cu(Ox)_2)^2$$

In addition, the 1:1 oxalate complex can protonate in acidic media:

$$(HCu(Ox))^+ \longrightarrow Cu(Ox) + H^+$$

At last, the oxalic acid is a weak diacid:

$$H_2Ox \longrightarrow HOx^- + H^+$$

 $HOx^- \longrightarrow Ox^{2-} + H^+$



Figure 2 : Concentrations of the various complexes involving Cu^{2+} in a solution containing 1 mM copper sulfate and 5 mM sodium oxalate.

Electrochemical Society Proceedings Volume 2003-26

The efficiency of the complexation process depends on the variation in the pH of the solution [1]. In the experimental conditions used here, where copper concentration is much lower than oxalate concentration, copper(II) gives no precipitate with oxalate in solution. Figure 2 shows () that the anionic $1:2 (Cu(Ox)_2)^{2-}$ complex predominates in solution in the pH range used here as an empirical law:

$$pH = 0.6 - 0.84 \log C$$

where C is the concentration of the oxalic acid.

Then the pH of the working solution ranges between 1.5 and 4.5.

EXPERIMENTAL

Experiments were carried out on rotating disc electrodes made from a copper rod (Johnson-Matthey, 5 mm in diameter). It was used in a three electrode cell with Saturated Sulfate Electrode (SSE) as a reference and a large platinum grid as counter electrode. Cyclic votammograms were plotted by using an Autolab (Ecochemie) potentiostat. Impedance measurements were carried out by means of a Frequency Response Analyser (Solartron 1250) in a large frequency range.

Cyclic voltammograms and impedance measurements were carried out in oxalic acid media. The solutions were deaerated by bubbling argon into the solution for 20 min before the experiment and above the solution during the experiment.

Cyclic voltammetry

Electrochemical behaviour of copper-oxalate complexes

A cyclic voltammogram done on a 1 mM copper (II) in sulphate medium at a carbon disc electrode is shown in Figure 3. Changes occured in the voltammogram when oxalic acid was added to the sulphate solution. In particular, the cathodic wave was displaced towards more cathodic potentials. However, the anodic peak is very





similar with or without oxalate anions. This observation shows that even if copper(II) is complexed in the oxalate solution, the cathodic processes occur through the reduction of the copper-oxalate complex to metallic copper, which can be dissolved at anodic potentials [2].

Electrochemical Society Proceedings Volume 2003-26

Influence of oxygen on the cathodic processes

Figure 4 shows the current-voltage curves of copper in 10^{-2} M oxalic acid in aerated and deaerated solutions at two rotation velocities of the rotating disc electrode. In aerated solutions, an oxygen reduction current plateau is observed, whereas in deaerated solutions no reaction occurs in the cathodic potentials up to hydrogen evolution.



Figure 4 : Current-voltage curves of copper in 10² M oxalic acid in aerated and deaerated solutions at 10 and 100 rpm.



Figure 5 : Current-voltage curves of copper in various concentrations of oxalic acid in aerated (top) and deaerated (bottom) solutions at $\Omega = 10$ rpm.

Electrochemical Society Proceedings Volume 2003-26

Figure 5 shows the current-voltage curves plotted at various oxalic acid concentrations in aerated (curve a) and deaerated solutions (curve b) by argon bubbling. This shows that the cathodic processes are diffusion limited due to oxygen reduction for any oxalic acid concentration. At low oxalic acid concentration the diffusion plateau was not reached in the cathodic potential range studied due to the ohmic drop.

Figure 6 shows 2 cyclic voltammograms in an aerated solution. Scan # 1 is obtained by starting at the rest potential (at zero current), going to cathodic direction up to -1 V vs SSE, and then to the anodic region back to 0 V vs SSE, i.e. going trough copper dissolution and back to the rest potential. Then, scan # 2 is plotted starting and going back to the rest potential. It is observed that, in aerated or deaerated solutions, the cathodic reactions for scan # 1 are limited to oxygen reduction for aerated solution and hydrogen evolution without oxygen. On the contrary, scan # 2 shows an extra cathodic wave due to copper(II) reduction, coming from the dissolved cations produced by the transient dissolution which has occurred during second part of scan # 1 [3].

$$Cu^{2+} + e^{-} \longrightarrow Cu^{+}$$
$$Cu^{+} + e^{-} \longrightarrow Cu$$

The same behaviour was observed in deaerated solutions.



Figure 6 : Cyclic voltammograms of copper in 10^{-2} M oxalic acid at $\Omega = 10$ rpm and at a 1 mV s⁻¹ sweep rate in an aerated solution.

At fixed anodic potentials, where copper dissolution occurred, large current drifts were observed. As an example, Figure 7 shows the current transient observed at -0.35 V/SSE in 10^{-2} M oxalic acid. It demonstrates that a species adsorbed on the dissolving electrode and almost blocked the dissolution current. This feature could be due to copper oxalate precipitation : this compound cannot precipitate in aqueous solutions but can do it at the electrode surface where the conditions are very different due to mass transport control.

325



Figure 7 : Current transient recorded on copper dissolution in 10^{-2} M oxalic acid at E = -0.35 V/SSE at $\Omega = 10$ rpm.

Impedance measurements

326

The electrochemical impedances were measured at cathodic potentials in deaerated solutions to avoid the influence of oxygen reduction. The concentration of oxalic acid was chosen sufficiently high to avoid the problems related to diluted electrolytes and a low concentration of copper sulphate was added to provide the copper cations [2].



Figure 8 : Impedance measured at various rotation velocities on copper in $10^{-1} M$ oxalic acid + $10^{-3} M CuSO_4$ in dearated solution at E = -0.8 V/SSE

Figure 8 shows the impedance measured at -0.8 V/SSE at various rotation velocities. At low rotation velocities a diffusion impedance is observed in the low frequency range. This demonstrates that the cathodic processes are diffusion controlled even in the absence of oxygen. In the high frequency range, a capacitive

loop related to the charge transfer resistance in parallel on the double layer capacity is observed.

Figure 9 shows the change of the impedance diagram with potential ranging between -0.6 and -0.9 V/SSE for a 1000 rpm rotation velocity of the rotating electrode. When the potential cathodically increased, the amplitude of the impedance decreased corresponding to an increase of the cathodic current.

At high rotation velocity, i.e. when diffusion is not a limiting factor, two low frequency loops remain. These capacitive and inductive loops were already observed for deposition of copper in chloride media. The capacitive loop has been generally ascribed to the reduction of copper(II) to metallic copper through an adsorbed reaction intermediate involving copper(I) (see reaction mechanism I) [4]. The inductive loop has been generally ascribed to anion adsorption [4]. The oxalate anions adsorbtion could be at the origin of the inductive loop.



Figure 9 : Impedance measured on copper in 10^{-1} M oxalic acid + 10^{-3} M CuSO₄ in dearated solution at $\Omega = 1000$ rpm.

In a second step, the dendrite formation conditions were investigated at, again, various acid concentrations and electrochemical conditions. Figure 10 shows copper dendrites formed in 84 min at the edges of a 40 μ m in diameter copper electrode. Dendrites are formed at the periphery of the micro disc electrode where the current density is the highest. Generally speaking, dendrites are more likely observed in dilute solutions.

By combining those two approaches, studies about the mechanisms for dendrite growth on copper structures in the oxalic acid aqueous solutions are in progress.

327



Figure 10 : Copper dendrites formed at the edges of a copper micro disc electrode in oxalic acid aqueous medium.

SUMMARY

The classic copper deposition occurs in two electrochemical steps, as following : Cu^{2+} + 2e^- \rightarrow Cu^+

 $Cu^+ + e^- \rightarrow Cu^0$

However, in the chloride media, copper reduction occurs through an intermediate species CuCl.

We supposed that in oxalic acid media, copper reduction to metallic copper may occur through an adsorbed reaction intermediate involving copper(I) and oxalate anion protonated : Cu(HOx), like in chloride solutions.

For the classic copper dissolution, copper gives copper cations. These copper cations are transported through the solution and redeposited on the cathode.

In oxalic acid media, the formation of copper oxalate complexes at the electrode surface occurs and blocks the current dissolution. We may notice that the compound cannot precipitate in aqueous solution but can do it at the electrode surface where the conditions are very different due to mass transport.

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Aqueous Cryogenically Enhanced Post Copper CMP Cleaning

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This paper describes the use of a hybrid cleaning technology consisting of a combination of CO₂ cryogenic along with conventional wet cleaning. The aqueous cryogenically enhanced (ACE) technology for post chemical mechanical polishing (CMP) cleaning is investigated for removal of the sub 0.3 µm slurry particles with greater efficiency than is possible with current wet cleaning only. This results in improved yield and reliability at 130 nm technology node and lower. The paper investigates particle removal from hydrophobic surfaces such as the back-end-of-line (BEOL) dielectric and cap films. CMP of SiLK, Coral, SiC and Copper were done with colloidal silica slurries. Post CMP cleaning of the wafers consisted of wet cleaning, followed by spin rinse drying and CO₂ cryogenic cleaning. The results indicate that more than half of the light point defects (LPD) larger than 0.2 µm left after aqueous cleaning and drying were removed by cryogenic cleaning even when the latter was done more than 48 hours after the wet clean and dry. The paper also investigates the effect of cryogenic cleaning on low k surface and bulk film properties and the interaction of the cleaning medium with surface being conditioned. The roughness of Copper is specially studied in the context of device performance.

INTRODUCTION

At the 130 nm technology node and lower, global interconnect delays have been found to increase with reduction in feature size. It is due to the fact that the RC delay constant is proportional to L^2/w^2 where L is the length of the line and w the width [1]. The increase in signal delay occurs since the length of the lines do not decrease going down to the next generation of chip design, while the width does. To compensate for the increase in the RC delay at the smaller line widths, low resistivity metals and dielectric constant materials will be implemented in Dual Damascene integration. Chemical-Mechanical Polishing (CMP) will be integral to this fabrication scheme and is the last step in the Damascene sequence. It creates the topography over which subsequent layers are deposited in a multilevel interconnect structure. Thus, post-CMP surface conditioning is critical to the proper functioning of such devices.

Conventional post copper CMP cleaning method is aqueous based and appears adequate for removing slurry additives such as corrosion inhibitors, passivators, surfactants, CMP reaction by-products, etc. However, it is inadequate for removal of the sub 0.3 μ m slurry particles for reasons previously published [2-4]. Additionally, the hydrophobicity of low k dielectric films further makes the removal of small particles by aqueous cleaning difficult. Thus, a hybrid cleaning approach consisting of a combination

Electrochemical Society Proceedings Volume 2003-26

of aqueous and CO₂ cryogenic cleaning or ACE cleaning is investigated in this work for improved post copper CMP cleaning.

CO₂ CRYOGENIC CLEANING

 CO_2 cryogenic cleaning works by expanding high purity liquid CO_2 initially at 850 psi and ambient temperature through a specially designed nozzle. The orifice in the nozzle atomizes the liquid CO_2 into droplets. During the expansion the pressure drops to atmospheric pressure, accompanied by Joule Thomson cooling and a subsequent drop in temperature. The sudden cooling of the liquid droplets freeze them, thereby turning a fraction of the droplets to solid CO_2 while the rest to gas. Thus the CO_2 exiting out of the nozzle is a mixture of solid and gas in a highly directional and focused stream.

The removal mechanism of particulate contamination is by momentum transfer by the solid CO_2 to overcome the adhesive forces of the contaminant on the surface. Once the particles have overcome the adhesive force, the drag force due to the CO_2 gas flow removes them off the wafer surface. The cleaning chamber also has N₂ purge through it, which acts as a curtain in preventing re-contamination of the wafer. There is yet another mechanism responsible for removing low molecular weight organic contamination from surfaces. A thin layer of liquid CO_2 is momentarily formed at the interface of the cryogenic particle and the substrate surface during the moment of impact. The liquid CO_2 can then dissolve the organic contamination. The mechanism of cryogenic cleaning is described in greater detail in [2, 4] by Banerjee *et.al.*

EXPERIMENTAL

Various blanket films such as TEOS-based PECVD silicon dioxide, Coral a Carbon-doped-oxide (CDO) low k film, SiLk an organic low k, SiC and Copper were used. The films were polished using a 2 step polishing sequence on a rotary polisher. The Copper and barrier slurries used in this work consisted of alumina and silica abrasives respectively. The polished wafers were then cleaned using the following ACE cleaning sequence: DI rinse – MCC2500 chemistry (Lam Research) with dual brush scrub – DI rinse – Spin Rinse Dryer (SRD) – CO₂ cryogenic cleaning. The wet clean with MCC2500 was done in the Lam Synergy[™] tool. The cryogenic cleaning in the ACE cleaning sequence was done in the Eco-Snow BOC WaferClean[™] 1600 system. The cryogenic cleaning was performed greater than 48 hours after the wet clean and dry due to the transportation of wafers between the SEMATECH and Eco-Snow BOC facilities. Such a cleaning sequence increases the complexity of particle removal due to the inherent viscoelasticity of the slurry particles. However, the intent in these experiments was to determine the feasibility of using ACE cleaning sequence in post CMP cleaning and not optimization of the cleaning sequence.

A KLA-Tencor Surfscan SP1TM was used to measure particles in the size range $0.2 - 2.0 \ \mu\text{m}$ on the wafer surface before and after cleaning for determination of cleaning efficiency. Several other measurements were also made to determine any effects by the cryogenic cleaning mechanism on the different films investigated.

RESULTS AND DISCUSSIONS

The optimum cryogenic cleaning temperature was initially determined with TEOS wafers, polished with colloidal silica slurry and subsequently cleaned using the ACE cleaning sequence reported by Banerjee *et. al.* [2, 4]. The cryogenic cleaning was done at two temperatures of 30 and 80 C. The results, indicated that at 30C the number of LPD's on the TEOS wafer decreased from 151 to 116, 23.2% reduction in defects, whereas at 80C the decrease is from 146 to 84, before and after cryogenic cleaning or 42.5% reduction. This is likely due to the thermophoretic effects on the particles at the higher temperature [5]. Subsequent ACE cleaning experiments with CDO, SiLk, SiC, and Copper wafers were performed in which the cryogenic cleaning in the ACE sequence was done at 80C.

Figure 1 shows the results of post CMP ACE cleaning sequence. Five wafers were polished and then cleaned in the sequence described in section II. The wafers polished and aqueous cleaned at SEMATECH in Austin, Texas, were dried and sent to Livermore, California for the cryogenic cleaning. Defects on the wafers after drying the



Figure 1. Silica particles on CDO before and after cryogenic cleaning in post CMP ACE cleaning sequence.

wafers and then again after cryogenic cleaning were measured both at SEMATECH and BOC EcoSnow using SP1. ACE cleaning of polished CDO wafers showed that $59\% \pm 3\%$ of light point defects (LPD's) larger than or equal to 0.2 µm left after the wet cleaning sequence were removed by cryogenic cleaning. Wafer number 3 had the lowest defects of 111 after wet cleaning. The cryogenic cleaning was able to further remove 62% of the defects from it thereby reducing the final number of defects to 42 LPD's of 0.2 µm and above.

Electrochemical Society Proceedings Volume 2003-26

Several film properties were measured before and after cryogenic cleaning to determine effect of CO_2 cleaning on film properties. The dielectric constant of CDO was measured by Mercury Probe before and after cryogenic cleaning to be 3.08 and 2.95 respectively. The values being within the measurement error, indicating no degradation in the dielectric properties of the material due to cryogenic cleaning. The properties of the bulk film was also analyzed before and after cryogenic cleaning by FTIR as shown in figure 2. The analysis showed that the CDO signature peaks of carbon-hydrogen, silicon-hydrogen, and silicon-carbon after cleaning were unchanged indicating no change in film composition.



Figure 2. FTIR spectrum of CDO before and after cryogenic cleaning

The surface roughness of CDO was measured using atomic force microscope (AFM), fig. 3, to determine if the cleaning process induce any roughness in the dielectric



Figure 3. AFM of CDO before (left hand picture) and after (right hand picture) cryogenic cleaning.

film. The 1.0 μm x 1.0 μm AFM scan shows that the root means square (RMS) roughness of the CDO measured before and after cryogenic cleaning were 1.67 A and

1.56 A respectively, a 7% decrease in roughness. This indicates that the cleaning mechanism did not induce significant change in surface roughness of the dielectric film.

Residual contamination in surface conditioning during microelectronics manufacturing process is critical and needs determination as much as the cleaning efficiency. In cryogenic cleaning mechanism, surface residue can arise from impure CO_2 or from the formation of carbonic acid formed when the humidity inside the cleaning chamber is high. In our experiments and process, the humidity is controlled to a dew point of -45C or less. Thus the possibility of formation of carbonic acid due to the interaction of CO_2 and water is non-existant. Nevertheless, blanket SiLk wafer was cleaned cryogenically and the surface surveyed by X-ray photoelectron spectroscopy (XPS). The XPS data identified two elements; Carbon and Oxygen since SiLk is an organic dielectric film. Figure 4 shows the XPS peaks for Oxygen and Carbon before and after cryogenic cleaning. The atomic composition of Carbon was 97.9% \pm 0.1% before and 98.0% \pm 0.1% and for Oxygen was 2.1% \pm 0.1% before and 2.0% \pm 0.1%



Figure 4. XPS peaks of Carbon (left hand picture) and Oxygen (right hand picture) in SiLk before and after cryogenic cleaning.

after cleaning. Thus there was no change in either the bond structure or the elemental composition indicating that the cleaning mechanism did not alter the surface film composition.

Post CMP ACE cleaning was investigated on hydrophobic SiC film following the polishing and cleaning sequences described in the previous section. Figure 5 shows the particle removal performance for six blanket SiC wafers. The average removal efficiency for 0.2 μ m particles and larger for the six wafers was 67% ± 2%. The six wafers had an average of 6,833 LPD's on them following the post CMP wet clean and dry. The large number of defects left is due to a non-optimized post CMP clean of the hydrophobic film. The contact angle of SiC is 81.2° [6] indicating that SiC is very hydrophobic and hence hard to clean by wet cleaning. Cryogenic cleaning on the other hand being independent



Figure 5. Silica particles on SiC cap film before and after cryogenic cleaning in post CMP ACE cleaning sequence.

of surface tension of the film but dependent only on the momentum transfer of the aerosol particles, is better suited for cleaning hydrophobic films. The data therefore shows that a significant number of LPD's were removed by cryogenic cleaning from the SiC film even when the cleaning was done more than 48 hours after the wet clean and dry.

The roughness of SiC and Copper wafers were determined using AFM. In the Damascene integration scheme the increase in roughness of SiC, or any other cap film, after post CMP cleaning is not of particular concern. However, the same is not true for Copper. An increase in Copper roughness could potentially be harmful since it could increase electron scattering and hence line-to-line leakage current. Figures 6 and 7 show the AFM images of SiC and Copper before and after cryogenic cleaning. The 10.0 μ m x



Figure 6. AFM of SiC cap film before (left hand picture) and after (right hand picture) cryogenic cleaning

334



Figure 7. AFM of Copper film before (left hand picture) and after (right hand picture) cryogenic cleaning.

10.0 μ m scan of SiC wafer showed a decrease in RMS roughness of 29% from 1.35 A to 0.96 A. The Copper wafer scan on the other hand showed a significant decrease of 49% in RMS roughness from 5.31 A to 2.69 A. This implies that the soft Copper metal was finely polished by the cryogenic cleaning process. Similar fine polishing effects have been patented by Bitting and Bowers [7] on gold coatings during CO₂ cryogenic cleaning of mirrors. Since the Copper – dielectric barrier interface is the weakest interface in electromigration, the reduction in Copper surface roughness may be desirable from a reliability improvement perspective.

CONCLUSIONS

A combination of aqueous and cryogenic cleaning technologies, as in an ACE cleaning sequence, shows improved post CMP cleaning over existing aqueous cleaning. The improvement in cleaning does not come at a cost of film damage. The surface roughness, dielectric constant, and bulk film properties remain unchanged for the dielectric films. The CO_2 gas appeared not have interacted with the low k SiLk film and leave residues after the cleaning process. The softer Copper film roughness is reduced by the cryogenic cleaning process rendering it more suitable for interconnects. Hence a combination of aqueous and CO_2 cryogenic processes should be investigated for post CMP cleaning in the advanced device fabrication schemes.

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335

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Electrochemical Society Proceedings Volume 2003-26

Organic and Metal Contaminant Removal

Electrochemical Society Proceedings Volume 2003-26

CHARACTERIZING ETCH RESIDUE REMOVAL FROM LOW-K ILD STRUCTURES USING AQUEOUS AND NON-AQUEOUS CHEMISTRIES

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ABSTRACT

Wet chemistry removal of post-etch residue from ILD/copper devices is achieved through both aqueous and non-aqueous media, as demonstrated by the performance of GenCleanTM and GenSolveTM [1], respectively. The success of these applications is directly dependent upon thorough characterization with demonstrations on fab tools. Analyses use SEM and EDS with follow-on cross-sectional CD measurement for material integrity and undercut. Substrate safety is proven by minimal etch rate and confirmed through ESCA/XPS suggesting only the top 3-5 atomic layers to be in a protective (reduced) oxidation state. Complete rinse and dry is observed by FTIR. Final processing of ILD/Cu device wafers is conducted on SpectrumTM batch and CapsuleTM single wafer cleaning systems [2], and supported by subsequent device electrical analyses.

INTRODUCTION

Popular spin-on varieties of low-K dielectric materials that are being considered for semiconductor integration include SiLK® [3,4]. As these structures are etched into patterns, residue is formed which must be removed prior to subsequent processing steps. In theory, residue removal proceeds by the leaching of impregnated metal and exposing underlying organic matter which can then be dissolved and/or rinsed away. The choice in chemistry will depend upon the nature of the material, device structure, and tool design.

Etching and Cleaning

The conditions by which a product is etched will determine the composition and quantity of residue present. Plasma etching of SiLK[®] may proceed by an ionizable gas such as argon with the addition of O_2 and N_2 , respectively, to enhance throughput and improve anisotropy [5]. As seen in Figure 1, attempts to balance these competing activities in two forms of SiLK[®] have been shown to cause residue irregularities across the wafer.



Figure 1. Post-etch residue variation across the wafer in dense and porous SiLK®.

During cleaning, the chemistry must selectively penetrate small spot areas, remove residue, and most importantly, completely rinse and dry to leave the area pristine clean. There is a risk in poisoning chemically amplified resist (CAR), as observed by aqueous alkaline chemistries [6,7]. As the pores of new ILDs increase with decreasing diameter, desorption and rinsing become even more challenging. In considering safer alternatives to CAR poisons, glacial acetic acid has been shown to improve copper cleaning [8].

Batch Wafer Processing

Conventional batch processing tools deliver filtered chemistry to the wafers and recirculate material back through the system. In Figure 2, the batch unit, SpectrumTM [2], is shown through its chemical processing chamber (CPC) and design layout.



Figure 2. SpectrumTM batch processing unit with CPC (left) and design layout (right).

The SpectrumTM integrates spray and immersion technologies. The system incorporates surface tension-gradient-dry capabilities for ultra clean drying. As indicated in Figure 2, the CPC rotates the wafers vertically with fluid flow from the side being fed by several heated tanks. After cleaning, the unit undergoes a spin-rinse-dry (SRD) cycle. Using dispense and rinse cycles measured in minutes, throughputs may reach 300 wph.

Single Wafer Processing

Single-wafer cleaning tools are designed with precision and tight tolerances to deliver chemistry, rinse, and dry the wafer in minimal intervals. In Figure 3, the CapsuleTM [2], is described by showing a cut-away (left) and a cross-section (right) indicating fluid flow.



Figure 3. CapsuleTM single-wafer processing unit (left) and fluid flow (right).

The CapsuleTM processing module is comprised of upper and lower rotors that encapsulate the wafer to create a controlled microenvironment. There are multiple delivery lines for process media and gases. The entire assembly is rotated at user programmable speeds ranging from 0-2000rpm. Once the chemistry is delivered, centrifugal force causes a thin boundary layer to form on the substrate while the excess is drained away. Cycle times are measured in seconds with throughputs up to 150 wph.

EXPERIMENTAL

Two forms of ILD were evaluated, dense and porous SiLK® with similar reticles and nodes measured at 0.25um and 0.18um, respectively. Patterned and blanket wafers were prepared by International Sematech in conjunction with Dow Chemical [9]. The wafer stack is similar for dense and porous SiLK® where the polymer is commonly spun onto a hard etch stop such as SiCN and capped with SiO₂[10].

Analytical equipment used in material characterization include SEM (Hitachi 4700), Energy dispersive X-ray Spectroscopy (EDS), and Electron Spectroscopy for Chemical Analysis/X-ray Photoelectron Spectroscopy (ESCA/XPS Physical Electronics Quantum 2000), and Fourier transform infrared Spectroscopy (FTIR - Nicolet instrument). Wafer cleaning tools include SpectrumTM and CapsuleTM, manufactured by Semitool, Inc. [2].

RESULTS

Residue Characterization

A post-etch residue profile along the trench side wall is determined by regional EDS. This is achieved by directing the electron beam from top to bottom and receiving material composition information for each region. Taking the EDS data of four (4) trench locations including 1) top, 2) middle-top, 3) middle-low, and 4) bottom, a plot is made showing relative atomic composition along the trench wall. The data in Figure 4 suggests metallic Si and Cu as part of the composition of the etch residue along the wall.



Figure 4. Graphics of EDS regional composition profiling along the trench wall containing etch residue. Comparison to a SEM of dense SiLK® ILD.

Non-Aqueous Cleaning

Metal complexation in solvent-based systems is effected by complexing agents such as alkaline additives. Amines and quaternary hydroxides were selected for their corrosion protection [11], rapid breakdown of cross-linked polymer [12,13], and ease of rinsing for CAR safety [7]. Some formulations and their results are given in Table 1 and Figure 5.

Formulation Chemistry Additive Results Cyclic Amine **Oxide Delamination** Α Amide **Oxide Delamination** B Amide Cyclic Amine + Halide С Cyclic Ketone Quat. Hydroxide Residue D Sulfoxide Quat. Hydroxide Clean/Definition

Table 1. Tested non-aqueous systems for post-etch residue removal from SiLK® ILD.



Figure 5. SEM photos of dense SiLK® ILD specimens following exposure to non-aqueous chemistries described in Table 1.

Formulation D (Table 1) was further evaluated with co-solvents, corrosion inhibitors, and surfactants, leading to a new series of polymer removers [13] and GenSolveTM 670, to be used for copper/low-K batch wafer processing [14].

Aqueous Cleaning

A range of aqueous systems were tested using SEM observations of certain key areas of the ILD structure as a basis for evaluating performance. Such characteristics are included as safety to copper, the oxide layer, and if the barrier layer (SiCN) at the base is exposed (clean). These chemistries are described in Table 2 and Figure 6.

Table 2. Results from aqueous solution removal of post etch residue on SiLK® ILD/Cu.

Chemistry	pH	Halide	Cu-Safe	Oxide Safe	SEM	Barrier	Residue
					Clean	Clean	
A	<2	N	N	Y	Y	N	Y
В	<6	N	N	Y	Y	Y	N
C	<6	Y	N	Y	Y	Y	N
D	6-8	Y	Y	Y	Y	Y	N
Е	6-8	Y	N	N	Y	Y	N



Figure 6. SEM photos of porous SiLK® ILD/Cu cleaning with aqueous formulations identified in Table 2.

The preferred aqueous formulation identified as D in Table 2 and Figure 6 was developed further by optimizing ingredients and adding complexing agents, inhibitors, surfactants, and defoamers. Tests on other ILD materials has resulted in the development of the product, GenCleanTM SWC 2200, for Cu/ILD single wafer processing.

Device Integrity Analysis

As indicated in Table 3, compatibility tests with GenSolveTM 670 on blanket films of electrochemical deposited (ECD) copper and SiLK® suggested minimal variation.

Table 3. Profilometry of ECD Cu and porous SiLK® after exposure to GenSolveTM 670 for 100hrs @ ambient and the process of record (POR) of 30min @ 60C, respectively.

Chemistry	Cu Thickness Variation	SiLK® Thickness Variation		
GenSolve TM 670	< 0.1 Å/min	< 2 Å/min		

Surface copper was evaluated against the POR for GenSolveTM 670 using ESCA/XPS. The top 3-5 monolayers, estimated at <100Å, was shown to be converted from adventitious Cu(II) to a reduced state of Cu(I) and Cu(0) [14].

Figure 7 describes cross-sectional analyses done on porous SiLK® ILD structures by three (3) methods, namely, direct cleave (N_2 used with Cu), resin/cleave and polish, and focused ion-beam (FIB). the latter two were used to confirm no undercut and define the stack morphology and material porosity (i.e. note oxide and SiCN bottom layer).





Critical dimension (CD) analysis was carried out using direct cleave with a CD SEM software program and plotted vs exposure (Figure 8). Results varied between 20-80 Å, as taken on dense and porous SiLK® ILD structures after exposure to GenSolveTM 670 meaured at 10% and 50% up from the bottom within the trench. This data is consistent with a cleaning process (i.e. residue removal = increase line width).





Figure 8. CD measurement of porous SiLK $^{\textcircled{B}}$ ILD structures as taken at 10% and 50% distance from the substrate up the line following exposure to GenSolveTM 670.

Process Development

The POR in producing a substrate that is free of stripper chemistry, GenSolveTM 670, and moisture is proven by FTIR for both dense and porous SiLK® ILD (see Figure 9).



Figure 9. FTIR showing direct and subtraction spectra of dense and porous SiLK® ILD blanket films following exposure to GenSolveTM 670.

Wafer Processing

Patterned dense and porous SiLK® ILD wafers were prepared for processing in automated cleaning tools. Wafers are segregated and sent to a SpectrumTM batch and CapsuleTM single-wafer processing unit, which was, plumbed with GenSolveTM 670 and

345



GenCleanTM SWC 2200, respectively. Conditions and the results are given in Figure 10.

Figure 10. SEMs of porous SiLK® ILD/Cu patterns, reference (left) and exposed (right).

Following the batch cleaning of dense SiLK® in a SpectrumTM unit, the wafers were shipped to International Sematech where they were metallized and measured for a variety of electrical parameters and compared to a reference subject that was not cleaned. Serpentine resistance was tested at a number of locations across the wafer and all exhibited similar reduction in value, consistent with a cleaning condition (see Figure 11).



Figure 11. Resistance for dense SiLK® following exposure to GenSolveTM 670 POR.

CONCLUSION

The success of processing aqueous and non-aqueous cleaning chemistries for removing ILD post-etch residue is dependent upon thorough material characterization and fab tool demonstration. Many analytical tools must be used to model how certain chemistries will interact with the device and predict the outcome in a fab processing unit. In this report, GenSolveTM and GenCleanTM were shown to remove post-etch residue from both dense and porous SiLK® ILD devices in process times ranging from under 90sec to 30min, respectively, when using the CapsuleTM and SpectrumTM processing tools.

346

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Keywords

Interlayer Dielectric (ILD) Critical Dimension (CD) Process of Record (POR)

Electrochemical Society Proceedings Volume 2003-26

REVERSING OF SILICON SURFACE AGING BY LAMP CLEANING

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ABSTRACT

Chemical composition of Si surfaces subjected to prolonged storage undergoes significant changes. In this study the accumulation of organic contaminants on Si surfaces and the removal of such organic contaminants using lamp illumination were investigated. It is shown that Rapid Thermal Cleaning (RTC) implemented using infra-red lamps can reverse the effect of "surface aging" provided that in the course of prolonged storage the volatile organics are not transformed into non-volatile compounds. As expected, the best results were obtained using a strong oxidizing ambient such as ozone.

INTRODUCTION

During device processing Si wafers are exposed to clean-room ambient or plastic container ambient quite often for extended periods of time. In the process, surface condition changes due to the accumulation of organic contaminants which then undergo chemical changes in the presence of moisture and other organic compounds. This "surface aging" may have an adverse effect on processes such as gate oxidation [1-3] and contact metallization and also may cause distortion of measurements of surface characteristics by ellipsometry or non-contact electrical methods. With the thickness of gate oxides in the CMOS gates approaching 1 nm even sub-monolayer levels of adsorbed organics is expected to cause accelerated breakdown of the gate dielectric [4]. Recent reports have also shown that organic molecules adsorbed on wafer surfaces can cause several undesirable effects such as unintended hydrophobicity, enhancement of surface roughness, haze formation and deterioration of epitaxial growth [5, 6]. Consequently, the process of surface aging must be controlled and reversed when needed.

There are different cleaning techniques suggested for removing organic contamination from the surface of Si wafers. The most common solution to remove organic contaminants at present is a series of wet processes. Ozonated deionized (DI) water rinse technique requires a dedicated wafer rinsing and drying capability. Other methods such as UV/air and UV/O₃ [7], UV/O₂ [8], and oxygen plasma require UV light or plasma capabilities. These methods may be technically too complex for the relatively simple task of organic compounds volatilization. Premise upon which this experiment was initiated was that simpler yet equally effective methods should be used to control organics. In our earlier experiments [9-11] we have demonstrated effectiveness of white

Electrochemical Society Proceedings Volume 2003-26
light illumination in controlling surface organic contamination. In the present study Rapid Thermal Cleaning (RTC) using infra-red lamps is investigated as a technique to reverse "surface aging" processes, focusing on the oxidizing strength of process ambient on cleaning efficiency and dependence of this efficiency on the storage time.

EXPERIMENTAL

The Si wafers used in this experiment were p-type, <1-0-0> with a resistivity of 1-5 Ω -cm. All wafers used were as delivered from the manufacturer in sealed polycarbonate boxes. A few wafers were taken out these boxes at a time for various studies. The "aging" process was studied by storing wafers after different surface treatments in different ambients. Hydrophobic surfaces were prepared by treating the wafers in a 1:100 HF: Deionized (DI) H₂O solution for 2 minutes followed by a 5 minute rinse in DI water. Hydrophilic wafer surfaces were obtained by a 2 minute dip in 1:100 DI H₂O followed by a 10 minute immersion in standard SC1 (12:3:2 DI H₂O:H₂O₂:NH₄OH) solution at 75°C and a 5 minute rinse in DI water. These wafers were then stored in poly-propylene boxes or ambient air. Unless otherwise stated poly-propylene boxes were used in this experiment.



Fig. 1 Schematic of the cluster tool used in the study

A commercial 200-mm RTP module installed on the four sided cluster from Primaxx Inc. (Fig. 1) was used in this study. The wafer temperature in this computer controlled module can be raised up to 800°C. In this experiment the RTC process was implemented in oxygen or ozone ambient at 300°C for 60 seconds in most cases. The effect of lamp cleaning on "heavy" organics was studied for different periods of time.

As demonstrated earlier [10, 11] measurement of contact angle gives an accurate picture of the chemical condition of Si surface at various stages of aging process. Hence the bulk of the results in this experiment were obtained by measuring the contact angle of a 20-30uL droplet of deionized (DI) water on the Si wafer surface. A commercial CAM-

Electrochemical Society Proceedings Volume 2003-26

Wafer-II contact angle meter that uses the sessile drop method for measuring contact angle was used for the purpose. The error in contact angle measurement due to evaporation of the droplet (10-20% in 3 min) is less severe than that due to spreading (100% in 2 min) [12]. Hence, all the measurements in this case were made within 30 seconds of the droplet contacting the Si surface. The repeatability of this system is reported to be ± 2 degrees in the manual mode and the accuracy ± 0.5 degrees. All measurements in this case were done manually. Other methods of surface characterization employed in this study include Thermal Desorption Gas Chromatography Mass Spectroscopy (TD-GC/MS) and X-ray Photoelectron Spectroscopy (XPS).

RESULTS AND DISCUSSIONS

"Aging" of Silicon Surfaces

In this experiment the evolution of organic contamination of the silicon wafer surfaces over a period of time was monitored. The adsorption of organic compounds increases the contact angle of the hydrophilic surfaces and decreases the contact angle of the hydrophobic Si surfaces typically feature a contact a contact angle in excess of 70° whereas hydrophilic surfaces have contact angles in the range of 5° when free of any organic contamination.



Fig. 2. Contact angle vs. storage time for wafers stored in box.

Fig. 3. Contact angle vs. storage time for wafers stored in ambient air.

Hydrophobic and hydrophilic wafers were stored in plastic boxes and ambient air for 45 days and the evolution of contact angle with storage time was measured at regular intervals. As seen from Fig. 2 there is a relatively rapid change in the contact angles of both types of surfaces during the first week of storage. This type of behavior is also observed for surfaces stored in the ambient air (Fig. 3) except that the rate of change of contact angle is somewhat faster than that for the surfaces stored in the box. The higher rate of change of contact angle for the wafers stored in the lab ambient air is attributed to the exchange of air in the lab compared to the quasi stagnant ambient in the box. The

Electrochemical Society Proceedings Volume 2003-26

initial surface conditions also determine rate of organic adsorption on the wafer surface. It is observed that rate of decrease of contact angle for a hydrophobic surface is greater than that of a hydrophilic surface. It has been shown that a hydrophilic surface attracts more polar hydrocarbon groups than a hydrophobic surface [13] and polar groups tend to have a low contact angle with DI water [14]. This results in the slower rate of change of contact angle for a hydrophilic surface. A hydrophobic surface is capable of retaining a greater percentage of the polar groups adsorbed on it making the surface more polar with time and hence decreasing the contact angle.

Based on Figs. 2 and 3 it is postulated that "fresh" wafer surfaces adsorb organics faster than "aged" surfaces, implying that the surface is completely covered with organics and certain equilibrium between the ambient and the surface is established in the course



Fig. 4. GC/MS spectra for hydrophobic and hydrophilic surfaces stored in a box.

of prolonged storage. The contact angle of both hydrophobic and hydrophilic surface after a prolonged storage (~45 days) stabilizes around 30° independent of storage ambient suggesting that the chemical make up of the Si surface regardless of the initial condition tends to be very similar after an extended storage (in this case ~45 days).

The results obtained with contact angle measurements were confirmed by TD-GC/MS analysis. Figure 4 shows the GC-MS spectra of hydrophobic (Fig 4a) and hydrophilic (Fig 4b) Si surfaces stored in plastic boxes for 50 days The global amount of contaminants as well as kind of species were found to be the same on both these surfaces confirming the contact angle measurements. The results obtained also indicate the presence of long chain hydrocarbons on the wafer surface. This suggests that the organic compounds with low boiling points which are readily adsorbed on to the

wafer surface are gradually replaced by compounds with higher boiling points in the course of prolonged storage.

Electrochemical Society Proceedings Volume 2003-26

Rapid Thermal Cleaning (RTC)

352

Effects of Multiple RTC Treatments. We have demonstrated in our earlier work that lamp illumination in ambient air is not effective in removing heavy organics from the Si surfaces. The focus of this experiment is to study the effects of multiple RTC treatments in ambient air on organic contamination removal. Figure 5a shows the effect of RTC treatment at irregular intervals of time. The experiment was performed on hydrophilic starting surfaces for the case of wafers stored in a box and wafers stored in ambient air after initial treatment in standard SC1 solution with a recipe described earlier. RTC in ambient air performed at random intervals of time after about two weeks of storage is not effective in restoring the surface to its original condition. This effect is believed to be the result of the transformation of volatile organics into non-volatile, long chain compounds.



Fig. 5. Effects of multiple RTC treatments in ambient air.

Figure 5b shows the effect of periodic RTC on refreshing the Si surface. The conditions for the RTC were the same as the previous case but it is seen that with periodic refreshing of the surface the efficiency of the RTC treatment in removing organics remains constant. The effect of multiple RTC treatments on hydrophobic surfaces was not investigated because the contact angle of such surfaces decreases after RTC treatment itself. Hence it is not possible to isolate the effects of organics in the case of phobic surfaces.

Effect of Process Ambient on RTC. Figure 5b shows that RTC in ambient air is effective in refreshing Si surfaces only if it is performed every 2 days. This part of the experiment was performed with focus on the effect of oxidizing strength of the processing ambient. Initial experiments were carried out with fresh wafers in a condition as received from the manufacturer. Two cases of process ambient were considered for the purpose, pure oxygen ambient and 6% weight ozone in oxygen ambient. Two sets of wafers from newly opened polycarbonate box received from the manufacturer were subject to RTC at 300°C

for different times and the results are shown in Fig. 6. The starting contact angle in this case ~25° is an indication of contamination of the wafer surface due to out-gassing from the shipping box (fresh hydrophilic surface should feature a contact angle below 5°). It is seen from the figure that a 1 minute RTC in ozone is sufficient to take the contact angle close to 0° restoring the surface to its original hydrophilic state. But for RTC in pure oxygen ambient it takes a longer time to refresh the surface. These results confirm expected correlation between cleaning efficiency and oxidation strength of the ambient. Figure 7 further shows increased oxidation strength of O₂ + ozone ambient by comparing the oxide growth kinetics at 500°C and 600°C in O₂ and O₂ + ozone.

In the continuation of this study the effect of RTC in cleaning aged surfaces was investigated. Three sets of wafers that were stored for ~ 2 years in a polycarbonate shipping box were used for this experiment. It should be noted that the box was opened and closed periodically thus exposing the wafers to the ambient air in the lab. The results in Fig. 8 show that the contact angle of the wafers before any treatment is 35° which is in good agreement with our earlier observations. The wafers were subjected to RTC treatment in three different ambients for various exposure times at 300° C. As seen in Fig. 8 there is not much difference between the process in ambient air and pure, but there is a noticeable difference in performance for the ozone ambient which decreases the contact angle consistently and rendering the surface hydrophilic after a 4 minute exposure. These results further substantiate the argument that oxidizing strength plays a major role in refreshing the surface.



and oxygen ambient

and O_2 + ozone oxidation

353

he efficiency of RTC treatment with increasing time of storage of wafers was studied. As seen in Fig. 9 the efficiency of the RTC treatment in ozone and pure oxygen ambients stays invariable at almost 100%, but for the ambient air case the efficiency drops significantly after only one day of storage. This drop in efficiency is obviously attributed to the difference in oxidizing strength between ozone pure oxygen and ambient air. It is also important to note that RTC being performed in a controlled ambient that is isolated

from the cleanroom ambient might play a role in the higher efficiency of the RTC treatments observed in this investigation.

Effect of RTC in Controlling Fluorine Contamination. The effect of RTC on the fluorine remaining on the surface after HF treatments was also investigated in this study. Two sets of wafer were cleaned with a 1:100 HF: de-ionized (DI) water solution followed by a DI water rinse. Wafers labeled "RTC" were subjected to treatment in ozone ambient at 300°C for 60 seconds and the wafers labeled "No RTC" were not subjected to any treatment. The samples were then analyzed by X-Ray Photoelectron Spectroscopy (XPS). XPS quantification was performed by applying relative sensitivity factors (RSFs) derived from a series of polymer and glass standards. These RSFs take into consideration the x-ray cross section and the transmission function of the spectrometer. The approximate sampling depth under these conditions is 25Å. The results of the analysis are summarized in Table 1.



It is seen from Table 1 that the sample "No RTC" has a higher concentration of F than "RTC" indicating that RTC treatment can also be used to reduce surface concentration of fluorine. It is also seen that, as expected there is a higher concentration of oxygen and lower concentration of carbon in the latter case. The exact nature of the process of reducing fluorine contamination by lamp cleaning is not clearly understood at this point.

Table 1 Effect of RTC on residual Fluorine

Sample	F	С	0	Si
No RTC	0.3	19.7	8.3	71.2
RTC	0.1	7.8	42.6	49.3

Electrochemical Society Proceedings Volume 2003-26

SUMMARY

The experiments carried out in this study demonstrated the differences in organic adsorption on Si surfaces for different surface and storage conditions. The results obtained also demonstrated that lamp cleaning is effective in removing organic contaminants accumulated due to the wafer storage for long periods. It was shown that oxidizing strength of the processing ambient plays a key role in defining efficiency of the surface refreshing process. The possible effect of RTC treatments in cleaning residual fluorine elements was also demonstrated.

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Electrochemical Society Proceedings Volume 2003-26

ADVANCED PHOTO RESIST REMOVAL USING O3 AND MOIST UPW IN SEMICONDUCTOR PRODUCTION

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<u>Abstract:</u> The removal of organic contamination and photo resist with sulfuric acid based mixtures is a well established but expensive process step in S/C processing. As a low cost alternative Ozone dissolved in UPW (Ultra Pure Water) has been found unsatisfactory due to limited availability of reactive O_3 at the wafer surface. The current work shows the feasibility of stripping photo resist in moist ozone environments in an open tank system using the Barracuda® module, among mass production conditions.

INTRODUCTION

The removal of organic contamination and photo resist with sulfuric acid based mixtures in today's S/C processing is a well established but expensive and non environmentally friendly process step. Replacing the peroxide in the SPM (Sulfuric Peroxide mixture, also denominated Piranha) mixture by ozone has shown comparable results for organic contamination, however for resists strip; the long recovery time of the bath after the strip is unsatisfactory [1,2]. As a low cost alternative, dissolved ozone in UPW has been investigated for cleaning of organic contamination including post ash flakes and photo resist removal. While principal feasibility could be shown in various types of equipment ,the low solubility of ozone in de-ionized water prevents efficient supply of the active radical. Even at sub-ambient temperatures the maximum solubility of ozone is in the order of 100 ppm only and cannot overcome the loss in reaction speed. Photo resist removal rate and repeatability, especially for pre treated(i.e. baked and/or implanted) resists is significantly worse than the SOM (sulfuric ozone mixture) or SPM alternatives. One proven possibility of using ozone for resist strip is to provide the oxidant in a moist atmosphere at elevated temperatures. While hydroxyl ions are necessary to initiate the reaction, the reduced or missing boundary layer at the wafer surface in a vapor will provide ozone concentrations in the percentage range directly to the resist surface even at higher temperatures. Good results have been successfully demonstrated in spray processor [3], but also revealed significant disadvantages with respect to particle contamination and defect density. Previous work [4,5] also demonstrated the feasibility of tank processors for moist ozone processing of photo resists.

In the current work, focuses on the implementation of ozone resist strip using immersion batch equipment in S/C production. A wet bench module has been modified to

Electrochemical Society Proceedings Volume 2003-26

accommodate hot ozone gas treatment in a controlled humid atmosphere (Barracuda® module). The experimental work was performed at ATMEL in Rousset, France, a manufacturer of state of the art flash memory products. The first milestone of this project was to confirm the principal feasibility to strip implanted and non-implanted I-line and DUV resists with the new Barracuda® Module under full production conditions. Furthermore, the strip rate process window has been evaluated, and an appropriate production process sequence has been defined. Finally the Barracuda® module/process has been set-up to process short loop and production wafer by replacing a standard SPM/SOM process.

TOOL DESCRIPTION

The Barracuda® (DIO₃) module was integrated in an already installed AWP 200 (Automated Wet Processor for 200 mm Wafer) from SCP. This configuration (Fig. 1) allowed the evaluation of the new module in a FEOL (front-end of line) production environment and a direct comparison with a standard SPM/SOM process.

Fig. 1: Configuration of the test equipment

SPM	SOM	ODR	DIO3	DMG	DMG

(QDR:Quick dump rinse, DMG: Marangoni dryer)

The core of the module was the quartz process-tank, which was capable to process a full batch of 50 coated wafers . The tank was heated by infrared heaters from the outside and sealed by a double-lid-system. Inside the tank, DIW spray bars and an Overflow rinse were used to wet and clean the wafer. Ozone gas was injected into the tank through a diffuser manifold.. To avoid residual resist marks on the edge of the wafer, the tank was equipped with a so-called 'wafer flip' system to change the contact points of the wafer with the carrier during the process. Residual O_3 , that was not decomposed during the process was sucked out from the tank with a membrane pump and destructed by a thermal ozone-destruction-system before it reached the main facility exhaust.

PROCESS DEFINITION AND BASELINE RESULTS

After the wafers have been placed in the empty quartz tank, stable process conditions are created, by heating the tank from the outside to 90 °C, while wafers are rinsed in a hot DI Water spray. Ozone is then introduced at concentrations of 190 mg /l at a flow of 15 l/min from bottom to top, to achieve O_3 saturation within one minute. After termination of the spray rinse, water evaporates due to the high temperature inside the tank, and the wafers are soaked in the moist ozone atmosphere for some time while the ozone continues to flow. The soak is interrupted by short additional rinses in order to keep the moisture level and periodically wash-off already cracked resist and byproducts. After the strip process, a final 3-min Overflow-Rinse in the same module displaces the O_3 atmosphere and removes remaining contamination. Clean stripped wafers are taken from the Barracuda® module to a Marangoni® dryer.

Electrochemical Society Proceedings Volume 2003-26

Basic performance tests were performed in order to define the optimum parameter settings; various DOE's were ran, on coated bare silicon wafers, using a KLA Tencor UV1280 for resist removal measurements and a KLA Tencor SP-1 for particle contamination. Variable parameters were O_3 concentration, tank temperature, spray rinse time, time interval between rinses, and final rinse duration. Responses analyzed were removal performances (strip rate, uniformity), particle performance, organic and metal contamination.

The highest strip rate (Fig. 2a) has been observed for a water temperature of $90(+/-5)^{\circ}C$ with the tank temperature in a comparable range. Figure 2b shows the impact of the hot DIW spray duration on the photo resist removal. The best efficiency was reached with 10s spray steps. During this time, the cracked photo resist from the surface was totally removed. For the time interval between the spray rinses, both strip rate and particle results define the best process. Although the removal rate was maximal at longer intervals some byproducts, created within the process, could not be removed with the spray rinse, when they dried off. A 20 second delay in-between the spray steps has been evaluated as the best compromise between the shortest time to clear and optimal mass transfer. Based on the obtained initial data a final OF (overflow) rinse sequence of 3 minutes was found appropriate for the process. No positive effect was visible after a longer rinse sequence.





Fig 3b: Strip rate for I-line resist

Using the results of the process window evaluation, Barracuda® process was fully characterized for various types of photo resist (I-line, positive. and negative DUV) and implant pre- treatments. The results are shown in Fig. 3a and 3b. Typical average strip rates for I-line are in the 600 nm /min range, which result in total process times of 13 - 15 min. for typical resist thickness of 1.2μ . Corresponding removal rates for DUV are around 100 nm/min for positive and 150 nm/min for negative resist types. No significant difference in removal rate could be observed with implant levels up to 1e14at/cm². Higher implant levels resulted in drastically reduced strip rate and could not be removed in a process suitable for production purposes. The repeatability of the process both from wafer to wafer as well as run to run was found to be within 5 - 10 %, which is absolutely sufficient for resist removal processing. Strip performance dependency on wafer load in the batch is satisfactory with a 15 % difference between a single wafer and a full batch of 50 wafers coated with photo resist.

Post strip contamination results for particles, metals and organics have been investigated in parallel to the photo resist removal testing. Results for metals and organics are shown in Fig. 4 in comparison to conventional SPM processing. While metals could not be detected within the detection limits of the VPD-ICPMS and TXFR, the carbon content does not differ for moist ozone or sulfuric peroxide resist strips (measured by TDGCMS). Thus no residual resist or byproduct are left on the wafer after the process.

Element [atoms/cm ²]		Fe	Ni	Cu	Zn	Na	Al	Ca
Contamination on Wafer [atoms/cm ²] Processed with and without resist		<1.8e ¹⁰	<1.3e ¹⁰	<0.76	e ¹⁰ <1.2e ¹⁰	<1.8e ¹⁰	<2.7e ¹⁰	<2.3e ¹
Organic Contami	nation							
Sample	Reference Wafer test without resi	ference Wafer for Processe est without resist withou		afer ist	Reference Wafer for test with resist		Processed Wafer with resist	
Desorbed mass (µg eq n-C ₁₆)	3,1		2,8		2,7		3,3	3
Surface Conc. 2,1x10 ¹⁴ (atC eq. n-Cyc/cm ²)		1,9x10 ¹⁴			1,9x10 ¹⁴		2,2x10 ¹⁴	
Roughness and O	cide Growing							
Roughness and O: Wafers processe	kide Growing d without resist	Teo	chnology	T	Reference		Sampl	e
Roughness and O Wafers processe Roughness (nm R	kide Growing d without resist MS)	Teo AFM	chnology		Reference 0.16		Sample 0.17	e
Roughness and O: Wafers processe Roughness (nm R Oxide thickness (kide Growing d without resist MS) nm)	Tec AFM Ellipso	chnology metry		Reference 0.16 1.48		Sample 0.17 1.53	e
Roughness and O Wafers processe Roughness (nm R Oxide thickness (Wafers processed	kide Growing d without resist MS) nm) with resist	Tec AFM Ellipso Techno	chnology metry ology		Reference 0.16 1.48 Reference		Sample 0.17 1.53 Sample	e
Roughness and O: Wafers processe Roughness (nm R Oxide thickness (Wafers processed Roughness (nm R	kide Growing d without resist MS) nm) with resist MS)	Tec AFM Ellipso Techno AFM	chnology metry Dlogy		Reference 0.16 1.48 Reference 0.16		Sample 0.17 1.53 Sample 0.17	e e

Fig. 4: Metal and organic performance of Barracuda process

Particle results with bare Si and PR coated wafers indicate particle neutral or better performance down to 0.12 μ particle size (Fig. 5). Repeated measurements have confirmed that the Barracuda® process does not require a cleaning step after the removal process, like SC1. This is a major advantage to moist ozone stripping in spray processors.

Electrochemical Society Proceedings Volume 2003-26



Fig 5: particles performances

PRODUCTION DATA

The goal of this project was to demonstrated the ability of Barracuda to be utilized as a production module, so that we ran structured short-loops (different levels provided by ALTIS,LETI and ATMEL) to check resist stripping capability on patterned wafers. Checked levels were post poly-Si etch and ash strip(Fig 6 top), post deep trench etch and ash strip (Fig 6 center), post contact etch strip (Fig 6 bottom) and dual gate strip.

For all of those cases, Barracuda gave the same quality as our POR, in term of cleanliness or oxide growth for Dual Gate.

Finally, we tested Barracuda process on $0.18 \mu m$ CMOS production wafers, $0.25 \mu m$ Flash and Smart Cards technologies. Throughout the fabrication process flow, we process half of the lot (13 wafers) with the Barracuda process to compare to our POR (SPM/SOM)

Electrical data as well as Yield showed that Barracuda could improve production results, most probably by lowering ionic and metallic contamination brought by SPM/SOM use.(fig 7)



360 E

CONCLUSION

It has been demonstrated that the Barracuda module and process was a feasible technique for semiconductors production. The key of the process is mainly the alternation of O_3 soak time, where the resist is oxidized, with water sprays that provide a clean surface by washing-off byproducts of the reaction. We obtained comparable results with our SPM/SOM process in term of cleanliness, together with improved Gate oxide quality. More over, tests on productions lots showed a positive impact on yield results.

Barracuda module and process could advantageously replace SPM/SOM by providing good process performances associated with a smaller footprint and an environmentally benign media.

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CLEANING CHEMISTRY WITH COMPLEXING AGENTS (CAS): CA DEGRADATION MONITORING BY UV/VIS-SPECTROSCOPY

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ABSTRACT

Single Cleaning Chemistry (APM+TM) is a potential substitute for the conventional RCA cleaning sequence by combining SC1 and SC 2 cleaning performances into a single treatment. Since complexing agents (CAs) have to be added and the cleaning performance depends on their chemical stability, their lifetimes have to be known. This study presents lifetime determinations by UV/VISspectrophotometry of the aromatic CAs DEHP and catechol in APM+TM and related cleaning mixtures (TPM and NC). A potential sacrifical agent effect of the organic base choline is discussed, since DEHP's stability in NC, expressed in terms of half-lifetime ($t_{1/2}$) of reaction observed exceeds that in APM+TM and in TPM. A correlation between *DEHP*'s stability and the H_2O_2 concentration of the cleaning mixture is also drawn. It was found that the H₂O₂ concentration begins to decrease when the bath age exceeds $4*t_{1/2}$. Additionally, an attempt has been made to highlight CA degradation pathways applying reaction mechanisms from literature.

INTRODUCTION

For the last four decades, the RCA sequence has prevailed in the wet chemical cleaning of silicon wafer surfaces. Today, more than 30 % of the overall process steps during DRAM production are wet cleaning steps, of which more than half are RCA steps. Hence the numerous attempts in recent years to optimize wet chemical cleaning. Flexible fabrication systems can be seen to emerge which fall back on single wafer treatment instead of batch processing (1). It is reflections like these that gave rise to new techniques like the ozon-based IMEC-CleanTM and that based on the conventional SC1 mixture spiked with complexing agents (CAs): Single Chemistry Cleaning, briefly APM+TM.

Conventional APM was originally developed to oxidize light organics adsorbed onto wafer surfaces. Later it revealed an excellent particle removal capability, which is considered to be its most important feature today. On the other hand its most serious drawback is, that metals which may also originate from the high purity process chemicals employed will either deposit as hydroxides in its alkaline pH regime or attach themselves to the silicon surface due to its negative ζ -potential (2). The addition of suitable CAs to APM could on the one hand prevent metallic contamination and on the other hand mobilize and redissolve contaminants already present on the wafer surface, as has been proven recently (3, 4, 5, 6, 7). This is the fundamental idea of APM+TM. Beside several economically advantageous aspects, the use of CAs makes it possible to reduce the surface concentration of metals to the levels required in the future by the semiconductor

362

roadmap (2010: $< 5*10^9$ transition metal atoms/cm², ref. 8).

CAs are already being widely applied during semiconductor fabrication today, for instance during copper CMP (9). In order to attain optimal performance, the stability of a CA employed in different kinds of process mixtures should be known. This work examines the stability of aromatic CAs employed in APM and alkaline APM-like cleaning mixtures (*e. g.* TPM and NC, where ammonia is replaced by non-volatile organic bases). The determination of CA concentrations were achieved with UV spectral photometry. The half-lifetimes ($t_{1/2}$) were then calculated from least square fitted time-dependent CA concentrations.

EXPERIMENTAL

The present study was performed with two well-known CAs (fig. 1), one of which, DEHP, is currently being discussed as a chelator in the treatment of iron overload diseases (e. g. β-thalassaemia, ref. 10). The UV/VIS absorption measurements were performed with a Varian Cary 100 spectrometer with a scan rate of 100 nm/min and spectral band width of 2 nm. The alkaline cleaning solutions were prepared without intentional metal spiking (fig. 2). Five different types of alkaline cleaning solutions were employed (volume fractions: base/30 % H₂O₂/H₂O): 1/4/20 APM, 1.65/1/5 NC (New Clean), 1.36/1/3.92 NC, 1.65/1/5 TPM (Tetramethylammonium hydroxide Peroxide Mixture) and 1.36/1/3.92 TPM. In NC and TPM ammonia of the original APM was replaced by a 2% stock solution of the non-volatile bases choline ([2hydroxyethyl]trimethylammonium hydroxide) and TMAH (TetraMethylAmmonium Hydroxide) respectively. The H₂O₂ concentrations of NC and TPM cleaning solutions were additionally adjusted to be equivalent to that in 1/4/20 APM, which resulted in the 1.36/1/3.92 composition. The preparations were carried out in boxes with laminar flow. The reactions were conducted in PTFE-vessels and the chemicals used were: CAs of either commercial p. a. grade or synthesized by us, 25 % NH3 (Merck, VLSI-SelectipurTM), 30 % H₂O₂ (Ashland GigabitTM), 50 % choline (Fluka, pract.), ~ 25 % TMAH (Fluka, purum), and 18.2 MΩ Millipore-water.



From a series of CAs, studied previously, *DEHP* and catechol were chosen on which we have focussed the stability study (3, 6). The CAs, which form 3:1 (ligand to metal ratio) metal complexes, were added to the solution to give a final concentration of ~ 3.2 mM (11). Prior to these stability tests, the CAs were tested to ensure their metal complexation in 1/4/20 APM at 50°C with Al^{3+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Zn^{2+} as monitoring

Electrochemical Society Proceedings Volume 2003-26

metals (3). In this connection it has been shown that the sequestration of AI^{3+} requires high CA concentrations.

The stability of the given compounds was studied in cleaning mixtures maintained at 35°C and 50°C. After preparation, samples of the mixture were taken as a rule every five minutes, transferred into Eppendorf caps and frozen immediately in liquid nitrogen to stop the degradation reactions. The samples were then either stored in a standard freezer at -22°C (short term storage) or in liquid nitrogen. To measure UV/VIS absorbance, samples were thawed and taken up in a buffer solution of pH 9.5 (NH₄Cl/NH₃) to bring their concentration within measuring range. To offset the strong H_2O_2 absorption, the measurements were performed against freshly prepared cleaning solutions without CA also taken up in a buffer solution (fig. 4). All measurements were carried out in scanning mode to detect possible decomposition species, however, none were found. The specific absorbance was read off within the standard deviation of absorption maxima of predetermined absorption bands which were determined from calibration measurements. The solutions for calibration curves were freshly prepared prior to each set of measurements. The mean values of absorbances with corresponding standard deviations from 3 repetitive measurements were converted to "total concentrations" (the sum of protonated and deprotonated species), normalized, plotted against sampling times and fitted using exponential regressions curves according to the following equation:

$$[A]_{t} = [A]_{0} * e^{-kt} \Longrightarrow t_{1/2} = \frac{\ln 2}{k}$$
[1]

where $[A]_t =$ total concentration at the moment t, $[A]_0 =$ total concentration at the beginning of the monitoring period and k = rate coefficient of the observed reaction. Equation [1] corresponds to rate equations of first- or pseudo-first-order respectively. The rate constant and the half-lifetime of CA degradation may be deduced from the regression curves.

In a different set of experiments, mixtures of TPM with DEHP were pepared in which TMAH was successively replaced by choline to study its potential stabilizing effect on the mixture. The molarity of the base in the mixtures was kept constant and based the value of 1.65/1/5 TPM (c[TMAH] = 0.0464 M). The stability contribution of choline was deduced on the one hand by means of the prolongation of CA's half-lifetime and on the other hand by titrimetric H₂O₂ concentration determination.

The H_2O_2 concentration of the cleaning mixtures was monitored by iodometric titration using 125 µl of the sample. The peroxide titrations should provide information about the so-called "delay times". The "delay time" stand for a period in which the initial H_2O_2 concentration of the mixtures remains almost constant.

RESULTS

Figure 4 gives an overview of typical absorption spectra of CAs employed in this investigation. In the wavelength range between 200 nm and 260 nm H_2O_2 behaves like a cut-off filter, as strong H_2O_2 absorption prevents the detection of sample peaks. For this reason and in order to extract CA's absorption bands from total absorbance, the spectra were recorded against a reference sample of freshly prepared cleaning solution. The thick black arrows in figure 4 point to two partly resolved absorption bands, which are typical for pyridin-4(1*H*)-one-type compounds in medium alkaline pH regime. The band at 280 nm is the neutral species (HA), whereas the one at 310 nm is characteristic for the deprotonated form (A'). The neutral form of pyridin-4(1*H*)-ones split up into several

Electrochemical Society Proceedings Volume 2003-26

tautomeric forms (fig. 3), whose absorptions overlay the absorption band 280 nm. In the case of catechol, the absorption band possesses a weak shoulder, which strongly indicates two overlapping bands.

Non-linear curve fitting of *DEHP* overall absorption spectrum between 260 nm and 340 nm with limitation to two absorption bands and assumption of gaussian peaks gives following parameters: neutral form absorbs at 278.53 ± 0.47 nm with a half-width of 32.07 ± 2.05 nm, whereas deprotonated species absorb at 315.91 ± 0.87 nm with a half-width of 16.03 ± 1.61 nm. In the case of catechol, the fitting results in the following values: maximum at 280.53 ± 1.15 nm, half-width of 31.62 ± 1.55 nm. The second band has its maximum at 295.09 ± 0.63 nm (13).



Figure 3: Three different tautomeric species of the neutral form of DEHP.



Figure 4: Absorption spectra of CAs investigated in 1/4/20 APM. The inset shows the total absorption spectrum of DEHP in NC recorded against a buffer solution. The characteristic absorption bands of *DEHP* and catechol correspond to $\pi \rightarrow \pi^*$ electron transitions.

Figure 5 shows the half-lifetime of *DEHP* in the cleaning mixtures APM, TPM and NC. *DEHP* has the highest lifetime in choline containing cleaning solutions, whereas TPM results in the least lifetimes of DEHP. Furthermore, DEHP is approximately 20 % more stable in 1/4/20 APM than catechol. On the assumption that choline is a potential reductant we investigated 1.65/1/5 TPM mixtures, where TMAH was successively replaced with choline in increasing moiety. An improvement in bath stability is taken as an indication for a prolonged CA lifetime. Figure 6 shows the half-lifetimes in this set of experiments. These preliminary results show that the half-lifetimes increase when moving from 1.65/1/5 TPM to 1.65/1/5 NC whereby the concentration of base is higher in TPM than in NC. In the case of "50 % TMAH-choline-peroxide mixture", the lifetime

365

has increased around 40 % compared to pure 1.65/1/5 TPM.









Fig. 7 shows the monitoring of the H_2O_2 concentration of the above mentioned cleaning solutions and the determination of the so-called "delay time". The "delay time" represents the period in which initial H_2O_2 concentration of the solution remains nearly constant. After the "delay time" is exceeded, the H_2O_2 concentration of the mixture starts to decrease significantly and which suggests that a large portion of the CA and potential products of reaction with sequestering capability have been exhausted. H_2O_2 concentration values higher than 1 may be explained by loss of water through evaporation during the reaction. The plot shows that a 1.65/1/5 TPM BLANK, this means without CAs, possesses no "delay time" under our experimental conditions. On the other hand, a 1/4/20 APM spiked with *DEHP* has the highest bath stability indicating the stabilizing influence of *DEHP*.

366



Figure 7: Titrated mean values of H_2O_2 concentrations and the standard deviations of three repetitive determinations from *DEHP* spiked cleaning solutions at 50°C. The lines indicate "delay times" of CA spiked solutions after which H_2O_2 concentrations fell rapidly.

Table 1 shows "delay times" estimated in relation to *DEHP*'s half-lifetimes. The "factor" in the last column demonstrates the number of CA half-lifetimes for which the initial H_2O_2 concentration remains nearly constant. In the case of *DEHP*, it is demonstrated that the cleaning solution will stay stable for approximately 4 half-lifetimes (threshold value) regardless of their individual compositions.

medium	"delay time"	half-lifetime	factor	
	[min]	[min]		
1/4/20 APM	250	60	4.17	
1.65/1/5 NC	> 200	80	n. d.	
1.65/1/5 TPM	100	24	4.17	
25 n% choline	100	22	4.55	
50 n% choline	140	37	3.78	
75 n% choline	130	34	3.82	
		Average:	41	

Table 1: "Delay times" of cleaning solutions deduced by iodometric H_2O_2
determination in relationship to *DEHP* half-lifetimes determined by UV-
spectrophotometry.

DISCUSSION

The experimental results reveal that DEHP spiked NC cleaning solutions possess the highest stability of all mixtures investigated: in 1.65/1/5 NC as well as in 1.36/1/3.92 NC

where the H_2O_2 concentration is equal to that of 1/4/20 APM. On the other hand, TPM cleaning solutions have the lowest stability of all mixtures. This is quite remarkable, as TMAH being less volatile is often used instead of ammonia in order to minimize loss of base. The reason for this order (TPM < APM < NC) could lie in the different chemical natures of the bases employed. Ammonia is known to be a relatively good sequestrant for copper and nickel and copper catalyses H_2O_2 decomposition. TMAH is not a CA itself, whereas choline while being a potential complexant may also become oxidized by H_2O_2 or by reactive oxygen species (radicals and singlet oxygen) which may form during catalytic decomposition of H_2O_2 (Haber Weiss mechanism). Preliminary results show a



Structure of betaine.

Figure 8:

positive influence of choline on the stability of cleaning mixtures. This positive impact of choline on the stability of cleaning mixtures has been demonstrated in a first trend (fig. 6). A common oxidation product of choline is betaine (fig. 8). Betaine possesses a structure that partly resembles the commonly used B-

aminocarboxylates EDTA and NTA. This structural motif may contribute to the enhanced stability of NC cleaning mixtures over those of APM or TPM, since betaine might be able to complex catalytically active transition metal ions.

The CA degradation focussing firstly on catechol may be interpreted as follows: in a first step, the catechol is oxidized to the corresponding ortho-(1, 2)-benzoquinone presumably via a semiquinone intermediate (radical anion). Two semiquinone species may undergo a disproportionation by re-formation of one molecule catechol and formation of ortho-benzoquinone. After the guinone has formed, the electrophilic carbon atoms of the carbonyl function may be attacked by nucleophilic reagents in the solution (e. g. ammonia, hydroxide and hydroperoxide anions) forming hydrates (geminal diols), α -amino alcohols and α -hydroxy hydroperoxides (perhydrates). Since relative nucleophilicity drops in the order of HO⁻ > NH₃ > H₂O (14) and since the nucleophilicity of the hydroperoxide anion (HOO) is about 200 times higher than that of the hydroxide anion, the formation of hydroperoxide adducts of the quinone should be favoured. The attack of hydroperoxide to ortho-quinone (α -dicarbonyl compound) leads to a ring fission product via a carboxylic acid anhydride which probably cannot be isolated (fig. 9, ref. 15). A similar reaction has recently been reported (16). Alternatively, 1, 4-addition on the conjugated carbonyl forming a hydroperoxide adduct is conceivable. Another degradation pathway could proceed via epoxidation of the conjugated carbonyl accompanied by nucleophilic cleavage of oxiran which would then result in the formation of a vicinal diol (glycol) or α -hydroxy- β -hydroperoxides.

With *DEHP*, the situation becomes more complex. The pyridin-4(1H)-ones may be generally represented by several tautomeric species (fig. 3). In medium alkaline pH regime, the speciation will then provide at least 5 different tautomeric forms which all differ in their oxidation potentials. The stronger the release of electrons from R1 and R2, the easier it is for the pyridinones to be oxidized. The formation of an radical of semiquinone-type similar to that of catechol is postulated (17).

It has been reported that the establishment of these tautomeric equilibria is slow (17). So, individual tautomers being more susceptible to oxidative breakdown than others may slow down the overall degradation rate, as they will not be sufficiently and quickly provided from other tautomers due to slow re-attainment of the species distribution.

Since H_2O_2 bears not only oxidative, but also nucleophilic potential, nucleophilic attacks at carbon atoms α , α' and γ of *DEHP* are conceivable (fig. 10). The nucleophilic attack on the pyridinone ring may result in ring fission and several degradation products thereof. One potential degradation product has been detected by HPLC/MS-coupling but not identified yet (18).



Figure 9: Potential degradation of catechol in alkaline cleaning mixtures.



Figure 10: First potential oxidation degradation steps of DEHP.

The results and conclusions can now be summarized: both compounds studied, catechol and *DEHP*, possess comparable lifetimes in 1/4/20 APM at 50°C. This is reasonable since *DEHP* (fig. 3) may be regarded as a catecholic-like compound. The nitrogen atom in *DEHP* behaves somewhat like an electron sink leading to a lower density of the π -electrons than in catechol which in turn may be a reasonable explanation for its slightly higher stability. Cleaning mixtures with choline possess an enhanced stability over those with ammonia and TMAH as bases attributable either to choline's potential sequestering capability or a "sacrificial agent"-related effect. The correlation of "delay times" deduced from peroxide titrations with CA half-lifetimes from UV-absorption determinations resulted in a constant factor, a threshold value, for which all *DEHP* spiked mixtures will remain stable.

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369

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ADDITIVE TECHNOLOGIES FOR SUB100nm DEVICE CLEANING

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ABSTRACT

For sub 100nm devices, we have to achieve cleaner surfaces without using strong chemicals and mechanical forces. It is important to utilize additive technologies to react/catch the targeted contaminants. Chelating agent technology can solve the cross-contamination problems caused by various metallic new materials introduced in FEOL. Surfactant technology is also very effective to remove ultra-fine particles under the condition of lower material loss (low temperature) and lower megasonic power. Surfactant technology is also effective to remove CMP slurry from hydrophobic SiOC surfaces.

INTRODUCTION

A wet cleaning process is required to achieve i) ultraclean wafer surfaces, ii) without any adverse side effect, iii) in short cycle time, iv) with high reproducibility, and v) with low Cost-of-Ownership. The requirement by the industry is becoming more severe and diversified along with further integration of ULSI (Figure 1). Numerous new



Figure 1. Technology Roadmap of Semiconductor and Challenges of the Cleaning Technology.

Function 1) Detaching Contaminants from Substrates

- For insoluble particles

- For soluble contaminants (Metal, Organic) => Dissolution

Function 2) Preventing Re-adhesion of the Contaminants from Liquid to Substrates

- For particles => Zeta potential control with alkali => Surfactant technology
 - For metals => pH / redox potential control => Chelating agent technology

=> Mechanical force

Function 3) Slight Etching

- For removing contaminants included in the film / the contaminants strongly bonded to the substrates by chemical bond



Figure 2. Essential functions required for removing micro-contamination.

materials are being introduced into the FEOL and BEOL. Some of these new materials are not so chemically stable in conventional RCA chemistry (1). Dissolved materials redepositing to other areas can cause serious cross-contamination problems. Essential functions required to remove micro-contamination are summarized in three functions shown in Figure 2. On the other hand, for sub 100nm device cleaning, we cannot use "several-nm-etching with conventional cleaning (in Function 3)" or "high-powermegasonics (in Function 1)" to remove fine particles any longer because they may cause device pattern damage. To achieve cleaner surfaces without using strong chemicals and mechanical forces, advanced additive technologies that can react/catch the targeted contaminants (to maximize Function 2) will become increasingly more important. Based on cleaning mechanisms for micro-contamination (2-5), advanced cleaning solutions for sub 100nm devices have been developed.

CHELATING AGENT TECHNOLOGY

For Preventing Cross-contamination Problems Caused by New Materials

APM (also called SC1, $NH_4OH/H_2O/H_2O$) cleaning is widely adopted in semiconductor process as it features good removal efficiency for particles and organic contaminants. One of the drawbacks of APM cleaning is that trace metallic impurities, if contaminated in the APM solution, adhere to substrate surface in large amount. This is caused by the dehydration reaction between the metal hydroxide and Si-OH (5). This problem can be solved by the chelating agent technology. The chelating agent can catch the metallic contaminants in the APM so as not to re-adhere onto the surface (4-6). This technology becomes more important to solve the metal-cross-contamination problems caused by various metallic new materials introduced in FEOL. As shown in Figure 3, the chelating agent can also prevent re-adhesion of the metallic contaminants derived from high-k or CoSi₂ gate materials.

Electrochemical Society Proceedings Volume 2003-26



Figure 3. Effectiveness of chelate-added alkali cleaning solution (MC1) in preventing Co or Hf adhesion from APM.

SURFACTANT TECHNOLOGY

For Accelerating Fine Particle Removal without Device Pattern Damage

For sub 100nm devices, it goes without saying that ultra-fine particles with a diameter of sub 100nm must be removed. Generally speaking, the smaller the particle size, the more likely to adhere (Figure 4) and more difficult to be removed (7,8). High temperature-10 minute-APM cleaning with megasonics can remove such small particles, but increases the loss of several nm of silicon and oxide and also causes damage to the sub 100nm device pattern. These problems can be solved with surfactant technology. A surfactant can prevent re-adhesion of fine particles and accelerate particle removal. This technology enables the removal of ultra-fine particles even under the condition of lower temperature and lower silicon and oxide loss (Figure 5). This technology is also effective to lower the megasonic power needed to remove particles (Figure 6,7). It is important to use the surfactants, which have no adverse side effects for the cleaning (such as remaining of organic residue, metallic impurity, or forming problem).



Figure 4. Potential energy changes when the particles with various diameters adhere onto the substrate surfaces (in the liquid medium. when the both particles and substrates are negatively charged).

Electrochemical Society Proceedings Volume 2003-26



MC1-SP = NH₄OH + Surfactant + Chelating Agent

Figure 5. Effect of temperature in removing ultra-fine particles. The surfactant-added cleaning solution (MC1-SP) can effectively remove the particles even with low temperature / low Si and Oxide loss.



Figure 6. Dependence of megasonic power in removing ultra-fine particles with 70°C-10min-APM (oxide loss: 1.3nm).



Figure 7. Dependence of megasonic power in removing ultra-fine particles with 50°C-10min-APM (oxide loss: 0.4nm).

Electrochemical Society Proceedings Volume 2003-26

For Single Wafer Application

Single wafer processing has significant advantages compared to traditional batch systems to dramatically reduce production cycle time. Single wafer processing speeds up processing time and therefore time to market. However, long processing time in RCA cleaning has been an obstacle for single wafer cleaning to be commercially adopted. The combination of the surfactant and chelating agent technologies is also effective for single wafer cleaning to reduce process time from the typical one hour DHF-APM-HPM to two minutes or less (9-11). Figure 8 and 9 shows the effectiveness of the surfactant/chelate-added chemistry. The particles lifted off from the substrate surfaces by the low-power megasonics are captured by the surfactant so as not to re-adhere onto the substrates. Simultaneously, the chelating agent catches the metallic contaminants. Basically, the number of cleaning steps can be reduced down to a single step with the surfactant/chelate added (modified) APM. To remove specific contaminants such as Al included in the



Spin cleaning, with Megasonic, 50°C, 30sec Particle Size : $0.1-0.2 \mu m$ Conventional APM: NH₄OH/H₂O₂/H₂O=1/2/80 AM1/H₂O₂/H₂O = 1/2/80

Figure 8. Effectiveness of AM1 (surfactant/chelate added cleaning solution) in removing particles (Single wafer cleaning tool: Applied Materials Oasis CleanTM).



Figure 9. Metal removal by single wafer cleaning with modified (surfactant/chelate-added) APM.

oxide film, a two- step process of DHF (0.3nm etch) – modified APM can be used. We do not need conventional methods such as 1nm etching with DHF because the almost all contaminants can be removed by the single step modified APM.

For Metal Gate Device Cleaning

376

A surfactant is also useful to clean the metal gate devices. The conventional APM cannot be applied for the cleaning since the peroxide will eat metallic W (tungsten) of the gate electrode. However, without peroxide, Si surface coexisted with W are eaten by the ammonium hydroxide. The surfactant can prevent such Si etching (Figure 10) and can help the particle removal (Figure 11).



Figure 10. Etch rate of various materials with alkali cleaning. The surfactant-added alkali solution (AM1) can reduce both W and Si loss during the cleaning.



Figure 11. Particle removal performance of the surfactant-added alkali solution (AM1) for W metal gate application.

For Post Cu/SiOC CMP Cleaning

The essential function for post Cu-CMP cleaning solution for SiOC generation is: i) to prevent Cu re-adhesion onto the SiOC surfaces, ii) to remove slurry derived particles within a short time, and iii) to improve wet-ability of the hydrophobic SiOC surfaces. The chelating agent is effective to reduce Cu contaminants without causing Cu corrosion. The surfactant technology is effective to improve the wet-ability of the SiOC surfaces so as to promote a surface cleaning reaction (12). The large amount of Cu and CMP slurry contaminants deposited on the hydrophobic SiOC low-k surfaces can be removed with the chelate- and surfactant-added cleaning chemistry which can change hydrophobic surfaces to hydrophilic (Figure 12, 13).



Figure 12. Contact angle of SiOC surfaces with the surfactant-added chemistry.



Figure 13. Effectiveness of the surfactant-added chemistry in removing Cu/Low-k slurry from hydrophobic Low-k (SiOC) surfaces.

CONCLUSION

For sub 100nm devices, we have to achieve cleaner surfaces without using strong chemical and mechanical forces. It is important to utilize additive technologies to react/catch the targeted contaminants.

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DEGRADATION OF OXIDE PROPERTIES CAUSED BY LOW-LEVEL METALLIC CONTAMINATION

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ABSTRACT

In this work we demonstrate the deleterious effects that part per billion levels of metallic contamination induce in the dielectric properties of thermal oxides grown on silicon. Unlike many previous studies, the contamination in this work was applied only following oxide formation. Further, energetic contamination process environments such as high temperature or ion implantation were not used. Equilibrium J-E_{OX} measurements were used to assess the degradation in oxide quality caused by exposure to cobalt, copper, nickel, and iron contamination using either an unintentional contamination mimic or by a plasma mimic process. Cobalt is observed to act in a fashion different from other metals at low ppB contamination levels, suggesting a different behavior of charge trapping or modification of the oxide conduction processes. A strong correlation is demonstrated between capacitor measurement results and non-contact oxide stress-induced-leakage-current reliability measurements.

INTRODUCTION

This work demonstrates the deleterious effects that inadvertent metal contamination may impose on dielectric quality and properties. Many previous studies have been performed wherein metal was incorporated into the silicon substrate to assess the impact of within-wafer contamination on succeeding device preparation and properties such as gate stack integrity [1]. Alternatively, metals have been implanted at various doses and high energy or driven into dielectrics by high temperature processing [2]. In the present study we apply controlled amounts of metal contaminants to clean oxide surfaces and then incorporate them into the oxide using methods intended to mimic routine IC manufacturing conditions.

Over the past few decades of IC manufacturing, metal has been used in increasing amounts. Future generations of devices will continue this trend in the form of increased interconnect applications of metal, novel devices such as FinFets will utilize metal in their gate stack structure [3], and for example nano-particle memory devices may use metal particles as floating electrodes for charge storage [4].

Electrochemical Society Proceedings Volume 2003-26

The dielectric quality associated with metallic contamination is assessed by measurement of current density vs. oxide field of forming gas annealed aluminum gate capacitors. The results of more than 100 capacitors per contamination condition demonstrate severe degradation to dielectric quality in all cases. The most severe effects were observed for cobalt contamination. Further, results using gate injection correlate with results observed using state of the art non-contact corona charge stress-induced-leakage-current reliability measurements of contaminated oxides wherein substrate injection was employed.

EXPERIMENTAL DETAILS

With increasing metal use in advanced device technologies, the risk of unintentional entrapment or incorporation of these materials in dielectrics has grown. In this work we address two possible scenarios that could lead to metal presence in dielectric structures. The first of these we denote as unintentional contamination mimic, or UCM. In this case metal contamination is present on the dielectric surface and becomes trapped by the deposition of a thin film over-layer. In the second scenario, metallic contamination is present on the dielectric surface and is driven across the layer boundary to just inside or into the bulk of the dielectric with the assistance of a field provided by ions on the surface as might occur in a plasma assisted process. The latter approach we term as plasma mimic or PM.

The metal contamination used in this work including copper (Cu), nickel (Ni), iron (Fe), and cobalt (Co) were applied as dilute solutions to clean oxide surfaces using a spin coating process. Each was obtained as atomic absorption standards and was diluted to the range from 10 ppB to 500 ppB used in this work using acid-washed volumetric flasks and ultra-pure water. This dilution approach was characterized using ICP mass spectrometry to ensure consistency. Fig. 1 depicts the average surface concentration obtained following spin coating of nominal 500 ppB solutions using vapor phase decomposition of the oxide surface. Note that for each metal, the average surface value is in the 10¹²cm⁻² range, with Fe and Ni always obtained at slightly lower values than Cu and Co. The uniformity of the spin-on metallic contamination method was estimated using spin coating with Na and non-contact mapping of the applied density. The spin approach typically produced a standard deviation of the areal density on the order of a few percent of the target value. For each UCM case, the applied contamination was capped with an evaporated aluminum film that was later patterned and etched with a wet chemical process. For the PM cases, the contaminated oxide surface was coated with corona charge to provide a surface electric field into the oxide near 2MVcm⁻¹. The contaminated and charged wafer was then heated to 170°C for 10 minutes followed by an acid wash in a water/HCl solution to remove any remaining surface metal. VPD values for oxides contaminated by Cu using this technique are shown in Fig. 2. A value for a reference wafer that was processed identically to the Cu contaminated wafers, omitting the metal spin-on step, is also shown with the Cu incorporation levels observed to scale with applied metallic dilution level. Fig. 3 compares the reference, applied surface contamination level, and the values after the PM contamination process for Cu and Co applied at a 500 ppB level. Note that the post-PM Co level is comparable to or just above the reference level indicating that at the present level of sensitivity of this approach we

380

cannot say that any Co has entered the oxide using the PM method. Fig. 4 shows SIMS data for Cu in a 150Å oxide on silicon following the PM contamination method. These results show that Cu has been driven across the entire oxide thickness and partially into the silicon wafer by this gentle process. Similar analysis of Co, Ni, and Fe oxides contaminated by the PM process showed no detectible levels of these species in the oxide by SIMS analysis.

Capacitors for $J-E_{OX}$ testing were fabricated using thick oxide that was etched to provide a nominal 100µm diameter thin-oxide region for testing and a thick oxide support for the probe pads. After cleaning and 70Å gate oxide formation the structures were contaminated with individual metallic solutions by either the UCM or PM approaches and then metal gates were applied and patterned. Following a solvent clean, all samples were given a 30 minute forming gas anneal at 450°C. For $J-E_{OX}$ testing, over 100 capacitors were tested at each metal contamination condition for each of the UCM and PM scenarios. $J-E_{OX}$ characteristics were obtained by ramping the capacitors into accumulation (-V for p-type substrates) under close to equilibrium conditions. To achieve the latter a delay time was used to allow the displacement current associated with each voltage step increase to subside prior to current measurement for J calculation.

RESULTS AND DISCUSSION

Typical J- E_{OX} characteristics are shown for ppB level Co contaminated capacitors in Fig. 5 for the PM case. A reference characteristic is shown along with the three characteristics of contaminated samples where each was chosen as representative of the 50% levels of the results for each case. Compared to the reference characteristic, the values of J vs. E_{OX} are strongly affected with increasing contamination level in the low oxide field region, at the field point where enhanced leakage begins designated as the Fowler-Nordheim Knee point, in the F-N tunneling region, and the field value at which dielectric breakdown occurs. These results were especially interesting in light of an absence of any detectable Co inside the oxide using the surface analysis methods presented in the experimental methods section above for the plasma mimic or PM case.

To simplify the analysis we have condensed this data by plotting the 50% data for the UCM and PM incorporation approaches as differences relative to the reference values. We address in order, the impact of each contamination type, level and method on the position of the F-N Knee, on the width of the F-N region of the J- E_{OX} characteristics from the onset of enhanced conduction to breakdown, and finally the effects on defect density.

Fig. 6a and b show the shift in oxide field at which enhanced current or F-N tunneling begin relative to the same current enhancement point in reference samples. Recall that for this and succeeding consideration the values used were the 50% values of the distributions of results obtained from over 100 capacitors at each condition. From the figure we see that for Ni, Fe, and Cu the observed trend is to shift the F-N Knee to lower field values relative to the reference values by as much as 1.6 MVcm⁻¹. The striking result here is that for Co the trend shifts in the opposite direction. At 10 ppB levels of Co contamination the position of the F-N Knee is shifted roughly 1 MVcm⁻¹ to lower values from the reference, i.e. comparable to the 50 and 100 ppB levels of the other metals.

381

However, at 100 ppB of Co the shift is smaller amounting to roughly 0.5 MVcm⁻¹ from the reference. Overall, these data suggest that metals lower the energy barrier for tunneling regardless of contamination method, yet for particular metals such as Co the degree of reduction is less at higher contamination levels.

Fig. 7 compares the magnitudes of the oxide field range, from the onset of enhanced conduction to the oxide field value at dielectric breakdown, and presents the results as the range of the reference samples minus the range of the contaminated sample. For the UCM case we see that Fe, Cu, and Ni values are close to the reference range, differing by at most a few MVcm⁻¹ at the highest Ni level. However, cobalt's range is as much as 4 MVcm⁻¹ smaller than the reference range, partially due to its knee shift behavior noted above. For the PM case, Co behaves in a similar fashion but the other metals approach higher differences in order from Ni to Fe to Cu. The latter dependence may suggest a sensitivity of these results to the PM contamination method that was not observed in the UCM case. This last point is further exemplified in Fig. 8. This figure shows the ratio of the defect density of contaminated capacitors, the number of failed capacitors/total area of all capacitors, to the defect density of the reference samples. Part (a) of the figure indicates a ratio from 2 to 8 times that of the reference with very little spread in the values by metal type. Recall that the expected level of metal on the surface for the UCM samples before gate deposition was on the order of 10^{11} cm⁻² to 10^{12} cm⁻² for each metal type. The level of metal incorporated into the oxide in the PM case should only be a few percent of this range. Hence, we might suggest that a saturation of effect exists for the UCM cases depicted here and although the maximum ratio is comparable for both the UCM and PM cases the PM ratios appear to scale in decreasing order from Cu to Co to Fe and finally to Ni. Consideration of Fig. 9 reveals a very similar dependence on metal type to that observed in Fig. 8b. However, in Fig. 9, the data was derived from a completely different set of experiments. In the latter, commercial oxides were grown to 150Å in an IC fab on high quality 200mm diameter substrates. These wafers were cleaned and contaminated by the PM method and then tested using a non-contact corona ion-based method that provides a stress-induced-leakage-current or SILC value in response to increasing stress fluence magnitude. Note that a significant correlation exists between Fig. 9 and Fig. 8b. The observation that Cu is most damaging in both cases is consistent with our understanding from results presented herein that Cu is likely to be distributed throughout the oxide film and within the silicon. Cobalt is also observed to highly affect the dielectric quality as seen by these two experiments, even at levels undetectable by traditional surface analysis methods.

CONCLUSIONS

Exposure of thin oxide to transition metals including Co, Cu, Ni, and Fe produces dramatic degradation effects in the dielectric properties of such oxides. All of these metals are under investigation for use in advanced circuits and future electronic devices. This work has shown that an exposure of an oxide surface to as little as 10 ppB of Co may shift the enhanced current region of J-E_{OX} characteristics to higher oxide fields while at the same time reducing the width of the region between the F-N knee and E_{BD} . A major finding of this work is a correlation demonstrated between state-of-the-art non-contact SILC measurements performed on plasma mimic contaminated oxides and the

382

results of exhaustive capacitor measurements in which the plasma mimic method was applied within the capacitor fabrication sequence. The SILC measurement requires no such extensive preparation and therefore is an excellent candidate for in-line metrology of these metals for IC fabs.

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Fig. 1. Surface density of metal following spin-coating of 500 ppB solutions.

Spin-on concentrastion, ppb

Fig. 2. Cu transported across the air/oxide interface by the PM method.

Electrochemical Society Proceedings Volume 2003-26



Fig. 3. Reference, as coated, and post-PM levels of Cu and Co in or on oxide.



Fig. 4. SIMS depth profile through SiO_2 and Si of Cu applied by the PM method.



Fig. 5. J-E_{OX} of representative reference and Fig. 6. three PM contaminated oxides with p different Co levels shown. c








Fig. 7. Reduction in F-N region $(E_{BD} - E_{knee})$ of contaminated samples relative to reference samples.





Fig. 9. Non-contact stress-induced-leakagecurrent (SILC) caused by metal contamination of oxide by the PM method.

CLEANING CHEMISTRY WITH COMPLEXING AGENTS (CAs): DECOMPOSITION OF CAs IN HYDROGEN PEROXIDE AND APM STUDIED WITH HPLC

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ABSTRACT

This study presents the application of HPLC with UV-VIS detection for the direct determination of the concentration of complexing agents in silicon surface cleaning baths. Direct concentration determination is necessary for evaluating the stability of a CA for application in APM+^M. The pyridinone-type complexing agents studied appear to react differently in APM+^M and hydrogen peroxide The monitoring technique presented could be applied to other complexing agents as well.

INTRODUCTION

Cleaning procedures are essential steps in the production of integrated circuits. The purity requirements are continuously increasing with each device generation. Semiconductor surfaces are principally cleaned by wet chemical cleaning. The classical wet cleaning bath is the RCA-clean (1). The RCA cleaning sequence comprises two steps. In the SC-1 step (standard clean 1), also called APM (=ammonia peroxide mixture), particles are removed and organic contaminants oxidized. The drawback of APM is the deposition of transition metal hydroxides on the surface and their subsequent inclusion in the silicon oxide layer formed. The oxide is then removed in a HF-dip, the short immersion of the wafer in dilute hydrofluoric acid. Finally, a new, clean oxide is generated in the SC-2 step by a hydrochloric acid / hydrogen peroxide mixture (=HPM) which prevents the metals from readsorbing.

The wet chemical cleaning described above entails the consumption of considerable quantities of expensive, semiconductor-grade chemicals and ultrapure water. One approach to reduce the consumption of chemicals, cleanroom space and process time by reducing the number of different cleaning baths is the single chemistry clean concept (2). In the approach studied in this work the SC-1 solution of the RCA sequence was modified to cover also the functions of the other baths. IMEC coined the trademark APM+TM for this particular version of single chemistry cleaning (3, 4). In the APM+TM concept, an appropriate chelating agent is added to the SC-1 bath that will form soluble complexes with the transition metals and prevent their precipitation as hydroxides from the alkaline APM+TM, thus making the SC-2 step redundant.

The complexing agents employed, being organic compounds, are decomposed sooner or later by the hydrogen peroxide. This limits the bath-lifetime of APM. An analytical

Electrochemical Society Proceedings Volume 2003-26

method for determining CA stability in APM+TM is needed. The methods reported to date have been indirect. In one such method residual transitional elements on a "cleaned" wafer are determined at different bath ages to give an indication of the amount of active CA still present in the bath. In another method the increase in the O₂ partial pressure arising from the decomposition of hydrogen peroxide is taken as a measure of the concentration of the CA present in a bath (5). We have investigated the application of two established analytical methods to the direct determination of concentration of the complexing agents in APM+TM: UV/VIS-spectrophotometry (6, 7, 8) and HPLC (2, 9). The concentration of the CA in an SC-1 solution vs time is taken as a measure of the stability of the CA. Apart from this with HPLC the products of decomposition, when separated, may be identified (using HPLC-MS), allowing for a better understanding of the reactions involved. At a later stage this could be useful for modifying the structure of the CAs to improve their stability.



Fig. 1. Pyridinones studied: alkyl, carboxyl, sulfonium and hydroxyl substituted

The CAs studied were selected from published works using such criteria as nontoxicity, high complex stability for transition metal ions and an uncomplicated synthesis which could be conducted under ultra clean conditions. The pyridinones were selected for their ability to form stable iron complexes and were originally designed to combat iron overload diseases in human beings (10). Iron is a common contaminant in cleaning baths; it catalyzes the the decomposition of hydrogen peroxide, thereby limiting the lifetime of the bath. The original design of the pyridinones had only alkyl substituents at the nitrogen atom. Different functional groups were introduced at that position to study their influence on CA-stability: carboxyl, sulfonium and hydroxyl functional groups, each linked by an alkyl chain to the nitrogen atom (Fig. 1). The pyridinones form complexes with M^{3+} ions in the ratio 3:1 (11).

EXPERIMENTAL

The stability experiments in hydrogen peroxide were conducted in small, closed PTFE vessels. The CA was weighed in the vessel and dissolved in 30 % hydrogen peroxide. The first sample was taken immediately after dissolution at ambient temperature and its concentration set at 100%. The temperature of the vessel and content was then raised to 70°C. The experiments in APM differed from this scheme in the detail that the PTFE vessels, containing the aqueous part of APM, were heated to the desired temperature before the experiment started. Ammonia, hydrogen peroxide and the CA, in the form of a concentrated stock solution, were added to the heated water at the start of the experiment.

Electrochemical Society Proceedings Volume 2003-26

The short timescale of the stability experiments in APM, compared to the timescale of the experiments in hydrogen peroxide, made it necessary to avoid the short period of undefined temperature while heating up the PTFE vessel. Samples were then taken from the vessel with an Eppendorf pipette at intervals of minutes in the case of APM and hours/days in the case of hydrogen peroxide. The samples were placed in Eppendorf caps, shock frozen in liquid nitrogen (-196°C) to prevent further decomposition and and stored at -22° C until analysis with HPLC. The samples were thawed only shortly before HPLC analysis. Samples in hydrogen peroxide were diluted and could be analyzed without further treatment. Samples in APM needed to be neutralized with formic acid prior to injection to avoid damage to the chromatographic column due to the high pH of APM. A stock solution of each CA was prepared and stored away from light at 8°C. These stock solutions of known concentration served to calibrate the HPLC-analysis.

The chromatographic separation was performed on a C_{18} reversed phase column of the size 150 x 2.0 mm, 5 μ m particle size, (Phenomenex). The HPLC instrument consisted of a P2000 gradient pump, an AS3000 autosampler, and a UV3000HR diode array UV spectrophotometric detector (ThermoFinnigan). The mobile phase was a water/methanol gradient with 2-20% methanol, the water containing 0.2% formic acid and having a pH of 3. The flow rate was 0.22 ml/min, the injection volume 20 μ l. The detection wavelength was 280 nm.

The complexing agents studied were synthesized in our group. The 30% hydrogen peroxide, 25% ammonia and the methanol were of Gigabit^M grade (Ashland). The UP-water was supplied by a Seralpur clean water system (Seral). The formic acid was of analytical grade.

RESULTS AND DISCUSSION

The stability experiments in 30% hydrogen peroxide were initiated by a cooperation with an industrial partner. The intention was to produce a hydrogen peroxide especially for APM+TM by adding the CA to the hydrogen peroxide at the source of production. The experiments were conducted at 70°C in order to shorten the duration of the experiments. A difference in stability among the pyridinone-type CAs with 4 different functional groups (Fig. 1) was observed (Fig. 2). The least stable of the 4 CAs, ECEHP (carboxyl substituent), was no longer detectable after 4 days, whereas ESEHP (sulfonium substituent) reached this point after 20 days. An influence of the functional group on the stability can be assumed since there was no other significant difference in the structure of the 4 pyridinones

The same 4 pyridinones were tested in 1/4/20 APM, i.e. a mixture of 25% ammonia, 30% hydrogen peroxide and water in the ratio 1/4/20, at 50°C. The temperature of 50°C, instead of the 70°C employed in the experiments in hydrogen peroxide, was chosen with reference to the industrial trend of reducing the temperature of cleaning baths. The intention in these experiments was to compare the different CAs and to obtain data under conditions prevailing in the industry. The bath lifetime of the pyridinones in APM was much shorter than in hydrogen peroxide alone, as was to be expected, considering that APM was developed for the removal of organic contaminants. Applying complexing

388

agents in this bath is especially challenging.



Fig. 2. Stability of CAs dissolved in 30% H_2O_2 at 70°C

The bath lifetime of the 4 pyridinones in APM (Fig. 3) was about two orders of magnitude shorter than in hydrogen peroxide. This difference in stability appears even greater if one considers that the concentration of hydrogen peroxide in 1/4/20 APM was 1.56 M, compared to 9.8 M in 30% aqueous solution and that the temperature was 50°C instead of 70°C. The other difference to the experiment in hydrogen peroxide was the relative stability of the pyridinones. In hydrogen peroxide it was ESEHP > DEHP > HPMHP > ECEHP. That order was changed to ECEHP > DEHP > HPMHP > ESEHP in APM.



Fig. 3. Stability of pyridinone CAs dissolved in 1/4/20 APM at 50°C



Fig. 4. Stability of DEHP in 1/4/20 APM at 35°C and 50°C

389

There has been a general trend in semiconductor cleaning to lower the concentration of the chemicals in and the temperature of the cleaning bath. This was due to the discovery that the cleaning performance of the «diluted APM» was not substantially lower and the roughening of the silicon surface was reduced. DEHP was tested in 1/4/20 APM at 35°C in order to assess its bath lifetime at lower temperatures. As expected, the bath lifetime of DEHP is longer at 35°C than at 50°C (Fig. 4). The use of CAs in semiconductor cleaning could become more common if the cleaning temperatures are lowered because the bath lifetime of the CAs benefits from lower temperatures.

Another modification of the original RCA-APM is the substitution of ammonia by other bases. Examples are cholin hydroxide and tetramethylammonium hydroxide (TMAH), their structures are shown in Fig. 5a and 5b, respectively. Unlike ammonia cholin and tetramethylammonium are not volatile and do not have to be replenished during the bath time (12).



Fig. 5a. Choline hydroxide



Fig. 5b. Tetramethylammonia hydroxide

The APM derivatives using those two bases have been designated NC (New Clean) and TPM (TMAH Peroxide Mixture). The stability of DEHP in NC and TPM at 35° C was determined and compared to that in 1/4/20 APM at 35° C (Fig. 6).



Fig. 6. Stability of DEHP in 3 different cleaning baths at 35°C. Sampling from the APM- and NC-bath ended after 200 min.

The new order of stability of DEHP was: NC > APM > TPM. The order of stability could be explained by the «sacrificial agent» model. According to it, an organic compound with a suitable redox potential could serve to protect the CA from oxidation by hydrogen peroxide by being oxidized in place of the CA. Cholin would then be a slightly better sacrificial agent than TMAH. The differences in CA-stability could also be explained by the ability of ammonia and cholin to form complexes with metal

ions, and TMAH lacking such ability. The bases ammonia and cholin support thereby the effect of the CA, lowering further the concentration of free transition metal ions. The metal ions catalyze the decomposition of hydrogen peroxide, generating hydroxyl radicals which accelerate the decomposition of the CA. TMAH, which forms no complexes, causes DEHP to have a lower stability in TPM than in NC and APM.

The different order of stability observed in hydrogen peroxide and APM (Fig. 2 and 3) could be explained by the difference in pH. Hydrogen peroxide had a pH of 6, APM of 9.5, respectively. In the alkaline APM medium the hydroxyl group of the hydroxypyridinone could be deprotonated, thus opening a new reaction path. Jammal (13) proposes two different, pH-dependent reaction paths which lead to identical oxidation products. He found that, in neutral and acidic solution, the anodic oxidation of DEHP starts at the lone pair electrons of the nitrogen atom in the aromatic ring. This pH is similar to that in the hydrogen peroxide experiments. The different substituents of the 4 pyridinones studied were attached to this nitrogen atom, hence the observed influence of the functional group is in agreement with the model of Jammal. In the second reaction path proposed by Jammal (13), the oxidation in alkaline solution takes place at the deprotonated oxygen atom of the hydroxyl group of the hydroxypyridinone. The pKa for the deprotonation of the hydroxyl group is 9.9. The decomposition in APM would then proceed by this path, thus the change in the relative stability of the CAs. This would explain the relatively small differences in stability of the 4 pyridinones which are identical in this moiety of their structure (Fig. 7).

Electrochemical Society Proceedings Volume 2003-26



Fig. 7. Structures and acid - base equilibria of DEHP as an example of the pyridinones

The chromatograms in Fig. 8 could support this interpretation. Decomposition products were found in both the experiments in hydrogen peroxide and in APM. The chromatogram of a pyridinone dissolved in APM or in hydrogen peroxide, ECEHP for example (Fig. 8), had several peaks. The peak at 2 min retention time is the peak of hydrogen peroxide which was not retarded on the reversed phase column and which has a UV absorption band at the detection wavelenght of 280 nm. The peak at 5 min corresponds to ECEHP. The small peak at 17 min was neither present in chromatograms of the stock solution of ECEHP nor in the samples taken at the start of an experiment. It evolved during the experiment and decreased after the CA was consumed. It has to be attributed to a decomposition product. The decomposition product in hydrogen peroxide and in APM appears to be identical since the chromatograms were similar. This would be in concordance with the model of Jammal which proposes that the intermediate products from the two different, pH-dependant oxidations, undergo rearrangement to form identical oxidation products. Clearly, there is need for further study.



Fig. 8. Chromatograms of ECEHP and its decomposition products. Sample taken from APM.

CONCLUSIONS

HPLC with UV/VIS detection is a suitable analytical method for the direct

391

determination of the concentration of complexing agents in APM+TM (9). Direct determination is necessary for evaluating the suitability of a CA for application in APM+TM. With HPLC the decomposition products of pyridinone-type CAs can be separated from the parent CA. The pyridinones appear to react differently in APM+TM and hydrogen peroxide, but they decompose to give similar products. It appears reasonable to assume that the method can be applied to other organic additives in wet chemical processes like CMP.

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Electrochemical Society Proceedings Volume 2003-26

CLEANING OF METAL GATE STACKS FOR THE SUB-90 NM TECHNOLOGY NODE

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ABSTRACT

Due to undesirable qualities of carrier depletion and boron out-diffusion utilizing polysilicon, dual-metal gate electrodes will be needed by 2007 (1). Some of the more favored candidate metals are TaN and TiN (2,3). The implementation of new materials into the process flow, especially at the Front End Of Line (FEOL), presents many challenges related to cleaning. In order to prevent cross-contamination between wafers in shared tools, it is necessary to remove the remaining residues from the backside and bevel of the wafer.

In this work it is demonstrated that by using a wafer spin-processor system, TiN, TaN and residues from mixed gate stacks on the backside, bevel and a defined region on the front side of the wafer were successfully removed as shown by TXRF results. In addition, optical microscopy, SEM, SP1 and profilometry provided pictures and graphs that show the accuracy of the removal of the metals from the front side.

INTRODUCTION

The 2002 update to the ITRS identifies replacement of the gate oxide (GOX) SiO₂ as one of the grand challenges in the next several years (1). Due to the resulting reliability issues from tunneling and gate leakage currents through the use of thin (<2 nm) GOX, high-*k* materials will be required. This will enable the use of a layer with a much larger physical thickness for an identical Equivalent Oxide Thickness (EOT). Since poly depletion also contributes to the EOT value, a new gate electrode material will also be required. Some of the more favored candidate materials are metallic compounds, e.g. TaN and TiN (2, 3). The implementation of these new materials into the process flow, especially at the Front End Of Line (FEOL), presents many challenges related to cleaning. In order to prevent cross-contamination between wafers in shared tools (metrology, lithography, etc.), it is necessary to remove the remaining high-*k* material, as well as metal residues from the backside and bevel of the wafer.

Electrochemical Society Proceedings Volume 2003-26

For this set of experiments, different stacks of blanket films were deposited on silicon wafers (CZ, <100>, p-type, 200-mm). The stacks were either composed of:

- (i) Physical Vapor Deposition (PVD) TiN or TaN deposited on a Si_3N_4/SiO_2 stack,
- (ii) PVD TiN or TaN on nitrided SiO_2 or
- (iii) poly-Si on PVD TiN or TaN on HfO₂ (as deposited).

Wafers were processed using the Backside & Bevel clean technique (4), on a SEZ SP203 wafer spin-processor system to remove the TiN, TaN and residues from mixed gate stacks on the backside, bevel and a defined region on the front side of the wafer.

EXPERIMENTAL

Sample Preparation

Silicon wafers (CZ, <100>, p-type, 200-mm) were given an IMEC-cleanTM in an automated wet bench. The stacks were composed of:

- (i) 50 nm LPCVD $Si_3N_4/250$ nm DXZ $SiO_2/100$ nm PVD TiN (or TaN),
- (ii) 4 nm CVD HfO₂/10 nm PVD TiN (or TaN)/100 nm poly-Si or
- (iii) 3.5 nm nitrided SiO₂/10 nm PVD TiN (or TaN)/100 nm poly-Si

on the front side of the wafers. In stacks (ii) and (iii), the wafer backside was previously protected with 15 nm $SiO_2/20$ nm Si_3N_4 .

Methodology

Etch rates of 100-nm metal gate blanket wafers were preliminarily determined by beaker tests with wafer pieces using a three-factor mixture design (Design Expert v.6.0.3) with varying percentages of aqueous hydrofluoric acid (HF), nitric acid (HNO₃) and ultrapure water. The optimal etch mixture, as well as additional chemistries, were then evaluated on a single-wafer spin processor of SEZ.

In this tool, the wafers are placed such that the process side is face up on a Bernoulli chuck. During the entire etch process the wafer floats on a nitrogen cushion without touching the rotating chuck, which allows wafers to be processed on one side without damaging the other. The chuck design permits a small amount of chemistry to wrap around the wafer to additionally clean the bevel and a defined area on the wafer front side. The depth of the removed zone on the wafer front side can be adjusted individually. For the results presented, 1.5-mm, 3-mm and 3.5-mm edge clearances were chosen. The chemistry can be run in re-circulation or single-pass mode. For the purposes of this work, the chemistry was re-circulated.

In the tests to verify complete removal of the metal gate, the front sides of the wafers were etched so the TXRF (Total Reflection X-Ray Fluorescence) spectrometer could be used for contamination measurements. For these tests, the wafers of type (iii) were etched down to the SiON. By using a thin SiON as gate dielectric, the wafers could be measured with a standard Si-calibration on the TXRF. Moreover, a better detection limit for Ti and Ta was achieved compared to wafers having high-*k* instead of SiON, because interference (e.g. between Hf and Ta) was avoided.

The undercut profiles (step height edge removal on wafer front side) were measured with a Tencor P-2 Long Scan Profiler. The sheet resistances of the TiN and TaN layers were measured using a Tencor OmniMap RS75/tc. A Leitz Ergolux microscope equipped with CCD was used for optical measurements. A Philips XL810 was used for SEM measurements. A TXRF 8300W from Atomika-FEI with MoK α excitation was used to measure the trace concentration of Ti and Ta on the wafers. A light scattering measurement system (KLA-Tencor SP1^{DLS}) was used for particle measurements on wafers.

RESULTS

Chemistry development

Initial etch rate evaluations were conducted on wafers with a thicker (100-nm) layer of the various metal gate materials without an additional layer of polysilicon. Recognizing that metal gate wafers could additionally include a polysilicon layer, the preliminary screening designs were conducted to determine if a polysilicon etch-type solution (HNO₃/HF/H₂O mixture) could be utilized as a single-pass chemistry to provide the desired backside removal, as well as bevel and defined edge clean of mixed metal residues. It was found that the etch rate of TiN was much lower than TaN and both were less than polysilicon.

Due to the considerable etch rate difference between TiN and poly-Si, for wafers with a TiN/poly-Si gate a long over etch of the poly-Si would be required to remove all TiN residue. To avoid the risk of damaging the backside, a two-chemistry solution was investigated. The target was to remove the poly-Si in a first step and then selectively remove the TiN. An APM-based chemistry ($NH_4OH/H_2O_2/H_2O$) at elevated temperature provided good etch selectivity between TiN and poly-Si.

Results with 50 nm LPCVD Si₃N₄/250 nm DXZ SiO₂/100 nm PVD TiN (or TaN) Wafers

First the backside and bevel of wafers with pure metal gates were cleaned. A HNO₃/HFbased solution was formulated to provide the complete removal of the TiN and TaN residues, respectively, from the wafer bevel and the 3-mm defined region on the wafer front side as shown in Figure 1 for the case of PVD TiN.

395



Figure 1 – Full wafer (right) and enlargement of bevel area (multiple microscope pictures next to each other) (left) showing 3-mm of TiN removed from bevel area of silicon nitride/CVD oxide/TiN wafer

Results with 4 nm HfO₂/10 nm PVD TiN (or TaN)/100 nm poly-Si

The next set of wafers included a thin layer of as-deposited (unannealed) HfO_2 as the gate dielectric material and on top a TiN/Poly-Si gate. With a second material present at the bevel, the clean of the front side edge has to be carefully controlled to avoid an under etching of the top layer. If the wraparound etch of the TiN or TaN would be deeper than the etch of the poly-Si, the risk of fracturing some of the poly-Si and subsequently creating particles would be very high.

A similar HNO₃/HF-based chemistry as previously used was able to remove the poly-Si and TaN residue from the backside, bevel and 3.5-mm defined edge of these wafers. As shown in Figure 2, the edge profile was again well defined without any undercutting of the upper poly-Si layer. The complete removal of the Ta residue from the wafer was demonstrated by TXRF measurements as discussed in the next section.

Due to the etch rate differences between TiN and polysilicon, a two-chemistry recipe was utilized to etch the $HfO_2/TiN/poly-Si$ wafers. The polysilicon residue was removed in a first step using a HNO_3/HF -based chemistry and the underlying TiN residue was subsequently removed selectively without additional attack on the polysilicon using the APM-based chemistry as shown in Figure 3. The effectiveness of this chemistry to remove Ti residues was demonstrated using wafers with a nitrided SiO₂ gate material and subsequent TXRF measurements as discussed in the next section.



Figure 2 – Edge profile on front side of $HfO_2/TaN/poly-Si$ wafer with 3.5-mm of gate material removed



Figure 3 – Edge profile on front side of HfO2/TiN/poly-Si wafer

A comparison of SP1 measurements (see Figure 4) pre- and post-processing demonstrated that the active area was well protected with only ca. 20 particle adders greater than 0.1 μ m ϕ_{LSE} .

397



Figure 4 – SP1 Particle Maps (5-mm edge exclusion; particles φ_{LSE} > 100-nm) of Pre/Post Processing of HfO_2/TiN/poly-Si

Results with 3.5 nm nitrided SiO₂/10 nm PVD TiN (or TaN)/100 nm poly-Si

As previously noted, it was desired to potentially utilize one chemistry to remove the polysilicon, as well as the metal gate material, from wafers containing both materials. The HNO_3/HF chemistry mixture utilized successively as reported in the previous sections was similarly applied to wafer stacks with a thinner layer of the metal gate (to be used as the work function material) capped with 100 nm of polysilicon. As shown in Figure 5, this chemistry was able to remove both the polysilicon and TiN gate materials from the wafer bevel and a 1.5-mm defined region on the wafer front side. The edge profile revealed that both materials were removed with the formation of a single step without undercutting the polysilicon layer.



Figure 5 – Edge profile (left) and multiple microscope pictures next to each other (right) showing 1.5mm of the gate material removed from the front side of a $SiO_2/TiN/poly-Si$ wafer

Removal of Ti and Ta residues

Electrochemical Society Proceedings Volume 2003-26

The effective removal of the Ti and Ta residues from the wafer surfaces was demonstrated by removing first the poly-Si and then the TiN (or TaN) layer from the front side of the Si/SiON/TiN(TaN)/poly-Si wafer stack and measuring the contamination levels with straight TXRF. As shown in Table 1, the metal gate residues could be reduced to the detection limits of the TXRF.

Chemistry	Ti	Та	
	concentration	concentration	
	[at/cm ²]	[at/cm ²]	
HF/HNO ₃ + APM	$< 8 \times 10^{11}$	N / A	
HF/HNO ₃	$< 4.5 \times 10^{11}$	$< 3 \times 10^{10}$	
Detection Limit	3×10^{11}	3×10^{10}	

I able I – 11 & Ta Residues Remaining After Etch of Wate	ning After Etch of Wafer	ning Afte	Remain	Residues	& Ta	- Ti	1	Fable
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CONCLUSIONS

Through use of the SEZ SP203 single-wafer spin processor and the selection of the appropriate chemistries, the backside, bevel and defined wafer front side area of mixed metal gate wafers containing TiN, TaN and polysilicon were successively processed. Profilometer results showed narrow step heights with no undercutting of the poly-Si layer. Measurements with optical microscope and SEM revealed good control of the defined undercut around the wafer edges. TXRF results demonstrated removal of the metal gate materials below the detection limit of the instrument and SP1 illustrated the effective protection of the active area during processing.

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Electrochemical Society Proceedings Volume 2003-26

PASSIVATION OF ALUMINUM AND ALUMINUM-COPPER ALLOYS IN **AQUEOUS ACIDS**

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ABSTRACT

The etch behavior of pure aluminum and aluminum copper (AlCu) alloy layers was studied in hot deionized water and in acidic solutions. For both materials, the etch rate is not constant in time. It was found that two dissolution mechanisms are responsible for metal corrosion. For pure Al, depending on temperature, it is controlled by dissolution rate of aluminum oxide and, because the solution saturates with aluminum salts, the etch rate decreases in time. For AlCu alloy the corrosion is oxidation limited. The surface concentration of Cu determines the cathodic corrosion current and, thus, the corrosion rate. During the etch process the surface concentration of copper increases and the etch rate goes up.

INTRODUCTION

One of the trends in Back-end of Line (BEOL) cleaning technology is the replacement of organic solvents by water-based solutions such as DSP (Dilute Sulfuric acid/hydrogen

Peroxide).¹ DSP is used for the removal of post-etch and post-ash residues after aluminum and via etch. In both cases Al is exposed. The process conditions are relatively mild, i.e., 45°C with 2 minutes process time.

Using inorganic acids for the cleaning of aluminum lines is counterintuitive as it is generally known that Al corrodes rapidly at pH lower than four, see Figure 1.² In this paper we will pose an explanation for Figure 1. Relation Al etch rate versus pH.

the corrosion inhibition of pure Al



and AlCu-alloy in sulphuric acid containing solutions by going further into chemical reaction mechanisms than in reference.³

EXPERIMENTAL

Experiments were performed on 4" and 6" silicon wafers coated with sputtered aluminum films containing either pure Al or AlCu with 0.4% Cu. Etch behavior of these layers was studied in several aqueous solutions where composition, process temperature, and process time were varied. Composition changes were made by the addition of 31% H₂O₂, 96% H₂SO₄, and 85% H₃PO₄. Exact conditions are summarized in Table 1.

Electrochemical Society Proceedings Volume 2003-26

solution	H ₂ SO ₄	H_2O_2	H ₃ PO ₄	T ℃	t min
DSP	8.4 %	3.8 %		35,45	2, 5, 10, 20
DSPh	8.4 %		0.5 %	35, 45	2, 5, 10, 20, 70
DS	8.4 %			35, 45	2, 5, 10
XDS	5.0 %			30, 45	2, 5, 10
HDI				75	2, 5, 10, 20, 30

Table 1. Overview of solutions and process conditions under study

DSPh-Dilute Sulfuric acid/dilute Phosphoric acid, DS: Dilute Sulfuric acid, XDS: eXtra Dilute Sulfuric acid, HDI: Hot Deionized Water

Al-thickness removed by the cleaning process was determined by measuring the concentration of dissolved Al in the solution by means of ICP-MS (Ion Coupled Plasma Mass Spectroscopy). For this purpose, the Al concentration was measured in 10-mL samples taken from fresh solution, and after one Al-coated wafer was immersed in this bath after several time intervals under conditions as mentioned in Table 1. The Al concentration in the solution in question was translated into film thickness loss by using a calculation factor for 4" and 6" wafers. The calculation of the factors is based on the mass of Al dissolved in the bath volume of 7 L. This method is more sensitive than the fourpoint resistivity analysis normally used for determination of metal layer thickness, because the detection limit of ICP-MS is about 1 to 70 ppt which corresponds to an Al thickness <1Å for 4"wafers. In contrast the four-point probe method delivers only reliable results after extremely long process times.

Some exposed aluminum surfaces were further analyzed by means of

- SEM (Scanning Electron Microscopy) to get information on surface morphology
- AES (Auger Electron Spectroscopy) for depth profiling of the Al-oxide thickness.
- ToF-SIMS (Time of Flight Secondary Ion Mass Spectroscopy) used at imaging mode to show the elemental distribution at the metal surface.

RESULTS AND DISCUSSION

Starting with hot deionized water (HDI) as process solution we find for pure aluminum and aluminum copper alloy different behavior. Pure aluminum starts with an etch rate that decreases as function of time (see Figure 2). It looks if saturation occurs

after 30 minutes. Aluminum copper allov starts at much lower etch rates with a clear increase after 20 minutes.

Studying the etch behavior of both film types in sulfuric acid containing solutions, again differences between aluminum and aluminum copper alloy are observed. In case of lower process temperature (30 and 35°C), a similar relation in thickness decrease/time is observed for pure aluminum. It starts with a certain etch rate, which decreases after 5 minutes to reach saturation later followed by XDS and DSPh as (75°C).



on. DSP shows the most rapid etch rate, Figure 2. Al and AlCu etch behavior in HDI

Electrochemical Society Proceedings Volume 2003-26



Figure 3. Al-etch behavior in H₂SO₄ containing solutions at 30 and 35°C.

Figure 4. Al-etch behavior in H₂SO₄ containing solutions at 45°C.

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7.5

10

presented in Figure 3. Comparing Figures 2 and 4 it is obvious, that the etch behavior of pure aluminum at 45 °C is similar to that of AlCu in HDI. The variant: DSP at 45°C is omitted in Figure 4 in view of its high etch rate.

Aluminum copper alloy shows similar etch behavior in sulphuric acid containing solutions as in HDI as well as at low and at higher temperature. At first, it is slowly etched with increasing tendency in time see Figures 5 and 6. In Figure 6 the DSP variant at 45°C is replaced by that at 35°C because of its high etch rate.





Figure 6. AlCu-etch behavior in H₂SO₄ containing solutions at 45°C.

For DSP and DSPh at 45°C also longer etch times were evaluated. As given in Figures 7, the results show for DSP after 10 minutes a further increase in etch rate for Aluminum copper alloy whereas for pure aluminum the etchrate stays constant. In DSPh (Figure 8) both materials show a constant etch rate after 5minutes.

Electrochemical Society Proceedings Volume 2003-26



Figure 7. Long time etch behavior of DSP

Figure 8. Long time etch behavior in DSPh

The results clearly show that distinct etch mechanisms are responsible for the different etch behavior of pure aluminum and aluminum copper alloy in hot deionized water, and in sulphuric acid containing solutions at temperatures below 35° C. Etching of pure aluminum is controlled by the dissolution of Al₂O₃. In water, the dissolution is inhibited by dissolved aluminum hydroxide and dissolution stops when equilibrium between solid and dissolved aluminum is reached at saturation. The solubility of Al₂O₃ is in case of HDI (75°C) at pH 5 to 6 about 10⁻⁶ to 10⁻⁷ mol/L Al³⁺ or AlO₂⁻, which corresponds to 0.15 to 0.73 ppb.² These data are in the same order of magnitude as the saturation levels in our experiments (saturation at 0.49 ppb). A similar saturation effect is observed for pure aluminum processed in acidified solutions at temperatures below 35° C. Here soluble



Figure 9. ToF-images of AlCu-fields: left Al image and right Cu.

compounds as $Al(OH)_2(H_2O)_4^+$ and $Al(OH)(H_2O)_5^{2+}$ are formed. The solubility of Al_2O_3 is reached at Al-levels between 1 and 3 ppb of Al for the solutions under study. With increased temperature the Al_2O_3 -growth controls the etch behavior. This results in constant aluminum etch rate in time.

For aluminum copper alloy the dissolution is clearly oxidation limited. Addition of an oxidation agent such as H^+ or H_2O_2 increases the etch rate considerably. AlCu forms a

galvanic cell, where copper is the cathode and aluminum the anode. The reduction of H^+ or H_2O_2 takes place at the copper sites. Aluminum provides electrons and goes anodically into solution. The etch rate of aluminum depends on the current density at the copper sites and, thus on the copper concentration at the metal surface. Both are low and small at process start resulting in low aluminum corrosion rate. It increases in time with increasing copper concentration.

The change in copper concentration at the surface can be observed with ToF-SIMS images. Therefore, copper and Al intensities on test structures were measured (see



Figure 10. Cu-images (ToF-SIMS) of AlCu - fields after several processes

the starting point for the etch process. In Figure 10 a gradually different Cu concentration on the AlCu-fields can be observed after a short process time. The pH and the etch rate of the solutions XDS, DSPh and DSP impact the surface Cu concentration. After longer process times, all examples show similar Cu-concentration on these fields. When processing these





thickness will not grow in time. In case of aluminum copper alloy the Cu-enrichment on the metal surface forms a shortcut of cathode current. That means, Al_2O_3 forms no large barrier and can grow.

Electrochemical Society Proceedings Volume 2003-26

Figures 9, 10 and 11). Figure 9 shows the surface images of non-cleaned test structures, where the illuminated squares consist of aluminum copper alloy. The left side shows A1 image and the right side that of Cu. Cu-levels on the AlCu-fields are not distinguishable from the area surrounding it and marks



Figure 11. Cu-images (ToF-SIMS) of AlCu-fields after HDI, 75°C, 30min.

test structures in HDI for 30minutes at 75°C no enrichment of the surface Cu concentration has been observed (Figure 11) and the surface is comparable to the starting point (Figure 9).

With AES-depth profiling of pure aluminum and of aluminum copper alloy after DSP treatment the aluminum oxide thickness can be determined. Figure 12 shows constant oxide thickness for pure aluminum and increasing levels for AlCu-alloy. In case of pure aluminum the Al₂O₃ forms a barrier layer hampering the oxygen and electron diffusion. That means the



Figure 13. SEM -images of metal surface after DSP-2min (top) and after DSP-15min (bottom).

High etching conditions cause a surface roughening of the metal as shown in Figure 13. The SEM-images of AlCu surface after 2 and 12 minutes processing in DSP at 45°C demonstrate the roughening effect, which is not found with the other solutions.

CONCLUSIONS

This study allows three main conclusions:

- The etch behavior of pure Aluminum and Aluminum Copper alloy layers is different because of distinct dissolution mechanisms
 - For pure Al the corrosion is controlled by the dissolution rate of aluminum oxide
 - For AlCu the corrosion is oxidation limited
- The etch rate of either materials is not constant in time. Therefore, etch rate determination based on one point measurement is unreliable.
- During process time typical for DSP-process, aluminum corrosion takes place very slowly. In case of pure aluminum, the reason is that the surface is protected by the low dissolution rate of Al₂O₃ and in case of AlCu by the presence of a small Cucathode area.

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Electrochemical Society Proceedings Volume 2003-26

BEHAVIOR OF ALUMINUM IN OZONATED WATER, OPTICAL AND ELECTROCHEMICAL STUDY

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Behavior of copper and silicon alloyed aluminum films in ozonated water was studied by immersion tests at different temperatures. The films oxidized slowly, thickness of oxide layer as well as sheet resistance of the films increased during oxidation. In addition, electrochemical behavior of aluminum was studied at room temperature and compared to that of silicon. Oxide layers of Al(Si) and Al(Cu) have porosity and their ability to prevent the further oxidation is poor compared to that of Si.

INTRODUCTION

Ozonated water has been used since last decade in microelectronics. It can be used in resist removal, organic contamination removal, and silicon oxidation. Applicability of ozone is based on its high oxidation power in water. Redox potential for the Eq. [1] is 2.07 V (1):

$$O_3(g) + 2H^+ + 2e^- \leftrightarrow O_2(g) + 2H_2O$$
^[1]

Ozone is capable to oxidize unsaturated organic compounds to carboxylic acids (2), which quite often are water-soluble. In comparison with conventional hot solvent or sulfuric acid processes ozonated water offers environmental and user friendly alternative for resist removal. Ozonated water process is also relatively fast, in the cleaning bench that was used in the present study resist removal rates 100-200 nm/min were achieved.

Since ozone is a powerful oxidant it is important to make sure that it does not oxidize metal layers under the resist. In the present paper we studied behavior of by far the most used metal in electronics, aluminum, in ozonated water. Oxidation was studied by immersion tests and electrochemical tests.

EXPERIMENTAL

Aluminum films were sputtered and they were alloyed with 0.5 % copper (Al(Cu)) or 0.5 % silicon (Al(Si)). The thickness of the Al(Cu) films was 150 nm whereas the Al(Si) films were 800 or 1000 nm.

Electrochemical Society Proceedings Volume 2003-26

Immersion tests

Immersion tests were carried out in Legacy immersion type bath. An ozone generator that produces ozone form oxygen by glow discharge is inside the bench. Gaseous ozone is dissolved in to water before the tank. Ozonated water is continuously circulated with a speed of 15-25 dm³/min. The ozone production of the generator is 280 g/m³ and the highest concentration in water was about 100 ppm, which was reached at 5°C. In the present study temperature was varied between 5 and 35°C. The ozone concentration in the bath was saturated to the limit achievable at the given temperature. It was about 100 ppm at 5°C, 70 at 15, 40 at 25 and 30 at 35. pH of the bath was around 5 and no additives were used.

The thickness of the oxide films was measured using Plasmos SD2302 ellipsometer. The instrument measures at the HeNe-laser wavelength (633 nm) and the angle of incidence is 70°. The thickness the oxide film is calculated by the ellipsometer from the measured Ψ and Δ values, when the refraction index (n) and extinction coefficient (k) of the substrate, and the refractive index of the oxide film are given. In the measurements of Al(Si) 1.308 and 6.203 were used as n and k, respectively. For Al(Cu) n was 1.07 and k was 6.28. Refractive index for oxide was 1.7.

FilmTek 4000 fiber-optic based spectrophotometer from Scientific Computing International was used to measure the reflectance spectra of the films. In the measurement reflectance data is collected in the 450-1650 nm wavelength range from normal and oblique (70°) angles of incidence. The software calculates the power spectral density from the reflection spectra. The film thickness can be determined from the statistically significant peaks of the power spectral density curves.

Morphology changes of the films were studied by LEO 1560 scanning electron microscope. GDOES measurements were carried out by Rautaruukki Oy with Leco SDP-750 spectrometer for Al(Si) films immersed 90 min in ozonated solution at temperature of 5 and 25°C. As a reference sample a sample without immersion was used.

Electrochemical measurements

Electrochemical measurements were carried out in order to study oxidation and dissolution rates of the aluminum films. Changes in the oxide layer were also investigated. Behavior of aluminum films was compared to that of silicon (N-type, (100), 1-10 Ω cm). The electrochemical measurements were done using open circuit potential measurements, Tafel method and polarization curves.

Polarization measurements were carried out using ACM Instruments Auto Tafel Potentiostat. Gaseous ozone was produced by a corona discharge GEV 5 laboratory ozonator type L220 -2.5/5.0, which produces ozone about 5 g/h. The ozone concentration of the gas mixture was about 20 g/m³. Concentration of ozone was saturated and it was about 25 ppm at 20 °C. Platinum was used as the counter electrode and calomel electrode (SCE) as a reference electrode in a vessel separated by Luggin capillary. Measurements were carried out in Avesta Cell (Fig. 1) without distilled water pumping through the filter paper as usual when Avesta Cell is used.

Electrochemical Society Proceedings Volume 2003-26



Figure 1. Avesta Cell and sample holder.

Measurements were done in distilled water and a dosage of 500 mg/l Na₂SO₄ was added to increase the otherwise too low conductivity of the electrolyte. Before experiments sample was washed using ethanol dried by warm air and placed in the cell. Electrolyte (150 ml) was added and ozone/oxygen gas was connected to the cell. Electrochemical measurements were started immediately. Scanning rate in polarization and Tafel experiments was 100 mV/min. In Tafel experiments samples were polarized after 10 min stabilization period cyclically150 mV to first to cathodic and then to anodic direction. Anodic polarization measurements were done after 60 min open circuit potential measurement.

RESULTS AND DISCUSSION

Immersion tests

Oxidation rate of aluminum films is dependent on the temperature of the bath. Figure 2 depicts thickness of oxide layer and sheet resistance changes at different temperatures after 30 minutes ozone process. The correlation between thickness and sheet resistance increase resistance is very clear although in the ellipsometric measurement the thickness result is strongly dependent on the fixed parameters and the correct value may not be found.





Increase in sheet resistance is due to the thinning of metallic film during oxidation. Since oxide layer is not thicker, some oxidation occurs also on the grain boundaries. In principle, aluminum could also dissolve as hydroxide species during oxidation. That is unfavorable due to pH of the solution. Aluminum hydroxides start to dissolve at pH below 4 or above 11. (3) Alloying of aluminum does not seem to have large effect on the oxide thickness. This is somewhat surprising since copper is known to dissolve in ozonated water. On the other hand, oxide composition, which was not studied, may be different between Al(Cu) and Al(Si).

At 5 and 15° C films were ozonated for different times (Fig. 3). Oxide thickness increases in the course of time. The behavior differs from oxidation of Si, which has been found to form thin, 10 Å passive oxide in ozonated water after 10 minutes. (4)



Figure 3. Oxide thicknesses and relative changes in sheet resistances after ozonation. Rs1 is sheet resistance before and Rs2 is sheet resistance after ozone treatment.

Figure 4 depicts reflectance spectra of ozonated Al(Cu) films. Trend is very similar to sheet resistance and oxide thickness measurements (c.f. Fig. 3). Thicknesses determined from the reflectances varied however from the ellipsometry measurements. According to them there is a thick 15-30 nm oxide on the film already before the

Electrochemical Society Proceedings Volume 2003-26

processing. This is probably not the case since according to GDOES, the oxide layer is below 5 nm and according to ellipsometer, which was measured 24 hours after oxide removal, it was only 1-2 nm, depending on the initial parameters.

For thicker oxide films reflectometry seemed to be suitable, however. At 25°C after 90 minutes, the same thickness, about 40 nm, was measured with both reflectometry and GDOES on 800 nm thick Al(Si) film.



Figure 4. Reflectances of Al(Cu) films ozonated for 30 minutes at different temperatures.

According to SEM the morphology of the films did not change during the oxidation at temperatures 5 and 15°C in 1 hour. On the other hand at 25 and 35°C color of the films turned yellowish and morphology changed considerably. Grains, which were very clear in the unprocessed aluminum films almost disappeared.

Electrochemical measurements

The behavior of Al(Si) and Al(Cu) films is similar in open circuit potential measurements (Fig.5). At the beginning of the experiment potential increases 200 - 300 mV and reaches a maximum after 17 min. After this potential decreases and reaches an equilibrium. This indicates that at the beginning of immersion the growth rate of oxide layers increases and the surface tends to passivate but the oxide layer formed is obviously not dense, but has some porosity and the dissolution continues. In comparison the potential of silicon wafer after oxide removal by HF increases steadily from about – 500 mV to -50 mV vs. SCE. The oxide layer on silicon seems to be dense and protective.



Figure 5. OCP measurements for Si, Al(Si) and Al(Cu), ozonated water, 500 mg/ $1\,Na_2SO_4.$

Figure 6 represents anodic polarization curves for Al(Si), Al(Cu) and silicon wafer after 60 min immersion in ozonated water. Current density of aluminum films is an order of magnitude higher than that of silicon. This indicates that also the dissolution rate of aluminum films is considerably higher than for silicon.



Figure 6. Anodic polarization curves for films in ozonated solution, sweep rate 100 mV/min), ozonated water, 500 mg/l Na₂SO₄.

In Tafel measurements the currents were very low and difficult to analyze. In figure 7 results measured for Si (without oxide removal by HF), Al(Si) and Al(Cu) are shown. The current density for silicon was $1.2 \times 10^{-5} \text{ mA/cm}^2$, for Al(Si) $5.5 \times 10^{-5} \text{ mA/cm}^2$ and for Al(Cu) $5.2 \times 10^{-5} \text{ mA/cm}^2$ respectively.

Electrochemical Society Proceedings Volume 2003-26



Figure 7. Tafel plots for Si, Al(Cu) and Al(Si), sweep rate 100 mV/min), ozonated water, 500 mg/l Na_2SO_4 .

Current densities for Al(Si) and Al(Cu) are almost similar. Current density for silicon is slightly lower. The measurement for silicon was done after 60 min stabilization at sweep rate 10 mV/min and after 10 min stabilization at sweep rate 100 mV/min for Al(Si) and Al(Cu). This may have a minor effect also on the results, but obviously it is not large, because the changes in the potential of Si in ozonated water is small.

The dissolution rates for test material calculated based data from Tafel experiments are according to Faraday's law for Al(Cu) about 0.57 μ m/a, Al(Si) about 0.54 μ m/a and for silicon wafer about 0.18 μ m/a.

CONCLUSIONS

In the ozonated water an oxide layer grows on the aluminum film. The layer thickness as well as sheet resistance of the oxide films grows in the course of the process time. The correlation between thickness and resistance is very clear. Aluminum film does not oxidize particularly rapidly; at 5°C sheet resistance of a 1 μ m silicon doped aluminum layer increased less than 0.7 % in 30 min. Corresponding oxide thickness was about 5 nm. Bath temperature as well as pH of the solution affects the oxide growth. At 25°C 16 nm oxide thickness and 1.2 % sheet resistance change were measured after 30-min ozone process. It is not favorable to change pH of the process. At lower pH oxidation of aluminum is enhanced and at higher pH ozone is too unstable.

412

The dissolution rates measured by Tafel method for Al(Si), Al(Cu) and Si wafer in ozonated solution at neutral region are all slow. Corrosion rates of Al(Si) and Al(Cu) are similar and slightly higher than that Si. Potential of the oxide formed on silicon is clearly higher than for Al(Si) and Al(Cu). Anodic polarization behavior of the test materials show that at higher potentials the corrosion rate of silicon is an order of magnitude lower than that of Al(Si) and Al(Cu).

The oxide layer formed on Si wafer in ozonated solutions is dense and protective and obviously thin. The dissolution rate of silica is very low. Oxide layers of Al(Si) and Al(Cu) may according to Pourbaix (5) consists of $Al_2O_3*3H_2O$ at neutral region. The dissolution rate of $Al_2O_3*3H_2O$ is low in pure water but higher than that of silica. Oxide layers on Al have obviously porosity and their ability to prevent the further oxidation is lower compared to that of Si wafer.

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INFLUENCE OF ALUMINUM BOND PAD SURFACE CONDITION ON PROBE-ABILITY

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ABSTRACT

This paper discusses the changes made in integrated circuit (IC) manufacturing process to improve probing of fine pitch aluminum bond pads. Surface condition of the bond pad has a significant influence on probe performance. The non-conductive film buildup on probe tips resulting in resistance increase between the probe and pads during sort is due to an oxygen/fluorine-contaminated film formed on the pad surface during IC fabrication. Optimization of the pad module resulted in a reduction in probe tip buildup. In addition, reduction in the pad hardness improved pad to probe contact.

INTRODUCTION

The chip size of sub-quarter micron device application-specific integrated circuits (ASICs) is often limited by bond pads. Benefits of smaller size devices in the silicon can be realized by reducing the pad pitch from above 100 μ m to 60 – 40 μ m range. These fine pitch pads create challenges for a manufacturable wafer sort process due to increased constraints on probing parameters such as probe wire diameter, probe force and over travel. An inefficient wafer sort process increases manufacturing costs due to quicker probe card deterioration and unwarranted yield loss as a result of poor probe to pad contact [1–4].

During sort, electrical contact is made to the pad as the probe breaks through the nonconductive film on the pad surface. Condition of this surface film will affect the quality of the contact, which can be quantified in terms of the contact resistance. Repeated probe touchdowns will lead to adhesion and accumulation of surface contaminants and pad material on the probe tip, affecting probe to pad contact. Quality of the electrical contact will have a direct effect on the input/output test signals. In order to obtain high first-pass yields, a good probe-pad contact with a low and stable contact resistance is required.

Device manufacturing has a strong influence on the surface condition of the pads. Presence of excessive fluorine and oxygen contamination on the pad surface is known to adversely affect wire bonding [5-7]. Our studies show that the pad surface condition will also influence wafer sort results. Bond pads are exposed to fluorine and oxygen plasma environments in the pad module during pad etch and post etch treatments. These fab

process steps are known to increase the thickness and adversely affect the chemical composition of the non-conductive surface film. Process improvements that reduce fluorine/oxygen content on the pad surface are shown to create probe-friendly bond pads. Pad hardness has also been shown to affect probe-ability of the pads. In this paper, experiments performed to study the influence of pad surface condition on fine pitch probing and process modifications made to improve probing will be discussed.

EXPERIMENTAL

Probing issues observed during the early development phase of sub quarter micron devices with 60µm fine pitch bond pads initiated the investigation into probe performance improvement. Probe sliding (Figure 1a) resulting in a poor probe-pad contact was observed on test chips. Optimization of the sort test conditions did not improve the poor probe-pad contact. Fab manufacturing processes were investigated to identify the cause for probe issues and to seek improvement in the fabrication of pads. The goal of the process changes was to reduce manufacturing overheads like offline/inline probe tip cleaning which reduce the sort throughput and probe card life time.



Figure 1a: Sliding of the probes on a 60µm Figure 1b: A good probe to pad contact is pitch pad is seen when the pad surface is hard.



made on a 60µm pitch pad with the manufacturing process changes

In this study, 200 mm wafers with a test chip that has 60µm pitch bond pads were used. Standard aluminum metallization with a stack of Ti/TiN/Al-Cu (0.5%)/TiN was used to create interconnects and bond pads. Process steps of interest are summarized below.

Summary of Process Flow

- 1. Dielectric deposition
- 2. PVD deposited final metal stack of Ti/TiN/Al-Cu (0.5%)/TiN
- 3. Patterning of metal lines

Electrochemical Society Proceedings Volume 2003-26

- 4. Passivation film deposition
- 5. Pad mask
- 6. Pad etch CF_4/CHF_3 based plasma etch; Note: TiN anti reflective coating is removed during pad etch
- 7. Pad ash resist strip in a O_2 plasma asher
- 8. Solvent clean
- 9. Furnace anneal in a N₂-H₂ gas ambient

Contact resistance, which is used as a measure of the quality of probe-pad contact, was collected in two different ways. Initially, contact resistance was measured using a PRVX[®] probe card analyzer. After the test wafer was probed on a LTX Trillium[®] tester, the probe card was taken offline and the contact resistance was measured between the probe tips and the tungsten check plate in the PRVX[®] system. Resistance shift from the baseline clean probe card data gives a measure of the amount of resistance increase due to contamination buildup on the probe tips. Since the measurements had to be taken offline with the PRVX[®] system, a quicker method to collect the resistance in the tester was developed. As shown in Figure 2, the probe card was modified with a grounded 130ohm resistor connected in series to alternate probe card pins. Since alternate pads in the test chip are shorted internally, resistance can be measured by forcing a current and measuring the voltage drop across two pins. The probes are repeatedly touched down on several die in the wafer and the overall resistance is data logged by the tester after every touchdown. Contamination buildup on the probe tips with every touchdown leads to an increase in the individual probe tip resistance, which was recorded as an increase in the overall resistance by the tester.



Figure 2: Schematic of the probe card setup used to measure contact resistance

The quality of probe marks on the pads was analyzed qualitatively through visual inspection with a microscope and was rated within a scale of 1 - 3 with a rating of 3 being good. Probe marks were considered good if the probe mark digs into the pad as soon as the contact was made and they were considered bad if the probe tips slid across the surface and barely made an impression on the pad.

Electrochemical Society Proceedings Volume 2003-26

RESULTS AND DISCUSSION

Probe Mark Quality

Quality of the probe marks is affected by the pad hardness and surface hardness of the pads [8,9]. Pad hardness is mostly determined by pad thickness, deposition conditions and the subsequent heat treatments while surface hardness is determined by the condition of the surface film on the pads. Experiments were performed on test chips to investigate the effect of several fab process factors that could affect hardness and probe quality.

Tests involving variation of the surface film condition did not have any affect on the probe marks. But a significant impact was observed with the variation in aluminum thickness. Figure 3 shows that hardness decreases with increase in the pad thickness and a significant improvement in probe mark quality is also observed. The reduction in pad hardness with thicker aluminum could be either due to change in the material properties of the deposited film or due to a decrease in the influence of the underlying hard dielectric film. Increasing thickness of the final level metal addressed probe sliding issues (Figure 1b) on products with fine pitch bond pads but the adhesion of contaminants and pad material to the probe tips with repeated touch down still caused continuity fails.



Figure 3: Effect of pad thickness on hardness and probe mark quality. Nano indentation method was used to measure pad hardness

Contamination Buildup on the Probe Tips

Auger electron spectroscopy analysis of material adhered to the probe tip (Figure 4) and the bond pad surface showed the presence of fluorine, oxygen and aluminum. The exposure of bond pads to fluorine plasma environment during pad etch will affect the presence of fluorine on the pad surface. In addition to the native oxide growth on

aluminum pad surface, the oxygen plasma exposure of bond pads during pad ash can affect the properties of the surface oxide. Experiments done on test chips to investigate the effect of varying degree of oxygen and fluorine exposure showed promising results. Figure 5 summarizes the results of different oxidation conditions. It shows that stripping the pad resist with a solvent clean (without any exposure to O_2 plasma) yields the lowest contact resistance with the least variation across wafer. Reduction in wafer temperature during ash also showed a decrease in contact resistance. The decrease in probe tip buildup could be either due to reduction in pad oxidation or due to a change in the adhesion properties of the surface film.

In order to study the effect of fluorine exposure of pads, TiN anti reflective coating on top of the aluminum and the pad etch time was varied accordingly. Reduction in the TiN thickness will result in a decrease of the pad over etch time and fluorine plasma exposure. Results in Figure 6 clearly show an improvement in contact resistance as a result of less contamination adhering to the probe tips.



418



Figure 4: Top view of a dirty probe tip (left) and clean probe tip (right) under a microscope



Figure 5: The overall contact resistance and variation of the resistance with multiple probe touchdowns is shown to improve with decreasing oxidation conditions. C-res was measured using the PRVX[®] probe card analyzer.

Based on the above information pad module was optimized for lower pad hardness and oxygen/fluorine plasma exposure by increasing the aluminum thickness, reducing the TiN thickness, pad over etch and stripping the pad resist with a solvent clean. Figure 7 shows the improvement in contact resistance due to process changes in the fab. Data presented elsewhere [10] shows that variation in the contact resistance was further reduced with the use of a non-abrasive online clean.



Figure 6: The overall contact resistance and variation of the resistance is lower with the reduced ARC TiN thickness and lower pad over etch time. C-res was measured with the modified probe card setup in the tester.



Figure 7: The variation in the contact resistance is significantly reduced with the process modifications. C-res was measured with the modified probe card setup in the tester.

CONCLUSIONS

In this study, it was shown that surface condition of the pads has a strong influence on the probe-ability of fine pitch bond pads and efficiency of the sort process. Probe sliding on bond pads was addressed with the reduction in pad hardness, which was accomplished with increase in the aluminum thickness. The amount of oxygen and fluorine present on the pad surface was reduced by optimization of pad over etch time and a solvent resist strip. Contamination buildup on the probe tips with multiple touchdowns was reduced with the reduction of oxygen/fluorine exposure of the pads. The material adhering to the probe tips with the new process was easier to remove using a

Electrochemical Society Proceedings Volume 2003-26

non-abrasive online clean. Significant improvement in first time pass yields was obtained even on older technology products with the above described manufacturing process modifications.

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OPEN CIRCUIT AND GALVANOSTATIC BEHAVIOR OF COPPER OXIDIZED AND REDUCED IN VARIOUS SOLUTIONS

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ABSTRACT

An understanding of the electrochemistry of copper allows optimization of aqueous cleaners used after a copper chemicalmechanical-planarization (CMP) process. The use of organo-silicate glass (OSG) low-k dielectric results in hydrophobic surfaces which are not cleaned well with de-ionized water alone. Use of complexing and chelating agents in the cleaning solution can impact the electrochemical behavior of copper. A common complexing agent used in CMP slurries and for staging solutions is benzotriazole (BTA) which minimizes copper corrosion but is difficult to remove. Post-CMP cleaning solutions have been developed which do not contain BTA but were designed to leave a passivating film on copper to minimize corrosion while the wafers await the next process step. Post-CMP cleaning formulation component selection was guided by the electrochemical behavior of copper. This paper will report the impact of components in several post-CMP cleaning formulations on the electrochemical stability of cupric and cuprous oxides.

INTRODUCTION

The use of copper in semiconductor manufacture has not ramped up as rapidly as initially anticipated. Numerous integration issues have delayed introduction of copper and low-k dielectrics. Copper is being used in production with oxide (TEOS), fluorinated-silicate-glass (FSG), and organo-silicate-glass (OSG) for the dielectric. The copper metal patterns are produced using an additive process, unlike the subtractive process used for aluminum; due to the inability to easily reactive-ion etch copper. As a consequence, a copper inlay process is used (i.e., Damascene) and the metal pattern requires a post-deposition planarization process. After the chemical-mechanical-planarization (CMP) process, copper contamination on the dielectric must be removed to minimize mobile ions which could result in dielectric breakdown. In addition, it is necessary to protect the exposed copper metal to minimize corrosion of the pattern during staging for the next process step. Consequently, specialized formulations have been developed for post-CMP cleaning applications which contain components to remove copper contamination from the dielectric surface and also protect copper patterns to avoid corrosion.

Electrochemical Society Proceedings Volume 2003-26

An understanding of the electrochemistry of copper allows optimization of cleaners for copper post-CMP applications. The corrosion process for copper involves both cuprous (Cu₂O) and cupric (CuO) oxides. In solution the copper metal is covered with a dense cuprous oxide film followed by a porous cupric oxide film (1). Corrosion of the copper occurs by diffusion of Cu⁺ or oxidizer through the cupric oxide film. The Cu₂O is oxidized to CuO. At high pH, CuO is readily converted to Cu(OH)₃⁻ or Cu(OH)₄²⁻ which are soluble. Benzotriazole (BTA) is a common complexing agent used to protect copper. BTA readily interacts with Cu₂O and forms a passivating film. Removal of BTA from copper surfaces has proven to be challenging. Cleaning products have been developed for surface preparation applications which remove BTA to eliminate down stream removal problems. Utilization of different copper passivators which form thinner films results in products which are capable of removing BTA but still passivate copper to eliminate corrosion while wafers are staged for processing to the next level.

EXPERIMENTAL

The working electrode consisted of a 5mm diameter copper rod from Alfa Inorganics which was 99.999% pure. The copper rod was potted in a piece of Teflon tubing using epoxy. The effective cross-sectional area of the electrode was 0.196cm². Prior to each experiment, the electrode was polished with ultrafine corundum (1500 grade), rinsed with DIW, and then gently wiped clean of any corundum particles. The electrode was shaken in the solution, if necessary, to prevent any bubbles from forming on the surface. The reference electrode was a silver-silver chloride (saturated KCl) electrode, and the counter electrode was a 1mm platinum wire separated from the solution by a course frit. Potentials are reported versus the Normal Hydrogen Electrode (NHE), corrected for the reference electrode potential offset. The solutions were made to the appropriate dilution with DI water and then immediately transferred to the cell under a stream of nitrogen gas. The dilution was typically 20:1 (5.00mL of the sample diluted to 100mL DI water). Measurements were made using a Princeton Applied Research Model 2263 Potentiostat.

The working electrode was oxidized at $\pm 1.00V$ for 5 minutes. Open circuit potential (OCP) curves were obtained by allowing the electrode to establish its equilibrium potential in the solution at effectively zero current flow (typically a few pico-amperes) for one hour. Galvanostatic curves were obtained by applying a reducing current of 10 microamperes to the working electrode and allowing it to establish equilibrium potential. The current was switched on immediately after the oxidation for some experiments; for others, it was turned on after a measured time (10 to 60 seconds rest time) had elapsed following the oxidation. The latter was done in order to see whether the copper oxide which had formed was affected by sitting briefly in the solution.

The thickness and weight of copper oxide formed was calculated from the Faraday equation, using the following input values:

Faraday Constant, $\lambda = 96,500$ coulombs/mole FW of copper (II) oxide, CuO = 79.5 FW of copper (I) oxide, Cu₂O = 143 Molar Volume of copper (II) oxide = 12.4 cm³/mole

Electrochemical Society Proceedings Volume 2003-26

Molar Volume of copper (I) oxide = $23.9 \text{ cm}^3/\text{mole}$

From the Faraday Equation,

Weight (grams) = (current)*(time)*(FW)/2* λ

Thickness (cm) = (weight)*(molar volume)*(1/FW)/electrode area

The initial copper (I) oxide weight was calculated by subtracting the weight of copper (I) oxide produced by the reduction of copper (II) oxide, from the total copper (I) oxide.

RESULTS

Of primary interest was the stability of copper oxides in various solutions. Figure 1 contains data for copper oxide thicknesses and their stability when they are produced in a dilute TMAH solution. The thickness of cupric oxide was about 8nm and that for cuprous oxide was about 17nm and little variation was observed as the oxides remained exposed to the solution for several minutes before reduction.



Figure 1. Oxide thicknesses remaining on copper as a function of time after oxidation in a 0.25% TMAH solution.

The data in Figure 2 indicates that by adding an appropriate complexing agent to the dilute TMAH solution, one can destabilize cupric oxide while having very little effect on cuprous oxide. The thickness of cuprous oxide formed was nearly identical to that shown

423

Electrochemical Society Proceedings Volume 2003-26

in Figure 1 at about 17nm, while that for cupric oxide was significantly less (e.g., 3nm versus 8nm) and was removed very quickly. Figure 3 contains data for the stability of



Figure 2. Oxide thicknesses remaining on copper as a function of time after oxidation in a 0.25% TMAH solution with a complexing agent added.



Figure 3. Oxide thicknesses remaining on copper as a function of time after oxidation in ESC 794 diluted 20:1 with DI water.

424

Electrochemical Society Proceedings Volume 2003-26

copper oxides in ESC 794, a post-CMP cleaner which contains both chelating and complexing agents. The thickness of cuprous oxide is less than that shown in Figure 1 and similar to that shown in Figure 2 (e.g., 3nm versus 8nm). Like the data shown in Figure 2, cupric oxide is removed very quickly with diluted ESC 794

Figure 4 contains oxide thickness data showing suppression of the reduction of cuprous oxide to copper due to passivators included in ESC T794M and ESC T794B. The Galvanostatic measurements were started immediately after oxidation. For ESC T794M and ESC T794B, the cupric oxide thickness was about 1/3 of that produced in ESC T794 (e.g., 1nm versus 3nm). The lack of cuprous oxide is due to the fact that it was complexed with the passivator and was not reduced. Processing with ESC T794B resulted in a passivating film that was less than 2.5nm thick and processing with ESC T794M resulted in a passivating film on copper that was much less than 2.5nm thick, and close to a monolayer in thickness (2).



Figure 4. Suppression of reduction of copper (I) oxide due to different copper passivators.

CONCLUSIONS

The electrochemical behavior of copper and copper oxides was investigated and used to develop dilute aqueous post-CMP cleaners. Products were formulated which removed BTA but were capable of passivating cuprous oxide, in some cases resulting in films that were quite close to a monolayer in thickness. Additives were investigated that stabilized or destabilized oxides on copper to alter the copper corrosion rate. Stabilizing the oxides

Electrochemical Society Proceedings Volume 2003-26

resulted in a reduction in copper etch rates. Destabilizing the oxides resulted in an increase in copper etch rates.

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Electrochemical Society Proceedings Volume 2003-26

AUTHOR INDEX

Agarwal, R. 108 Anttila, O., 195 Aravamudhan, S., 378 Arnauts, S., 145 Asselin-Degrange, E., 355

Baiya, E., 42 Banerjee, S., 328 Barbe, J.C., 153 Barnett, J., 93, 100 Bartosh, K., 305 Baum, T., 222 Beaudoin, S., 176 Beaudry, C., 23 Beck, R., 87 Beckx, S., 67 Bersuker, G., 93 Besson, P., 153 Boelen, P., 23 Brown, E., 305 Brown, G.A., 93 Broussous, L., 271 Burnside, K., 413 Busnaina, A., 190, 311 Butterbaugh, J., 116 Caymax, M., 67 Chabli, A., 355 Chang, C.K., 27 Chang, F.-M., 78 Chang, K., 78, 108, 347 Chaudhary, N., 93 Choi, S.J., 129

Christenson, K., 182

Clech, M.-C., 355

Conard, T., 67

Corsetti, T., 413

Claes, M., 67 Clark, S.C., 254

Danel, A., 153, 246, 271 Daviot, J., 246, 271 De Crecy, F., 153 De Gendt, S., 65 Delabie, A., 67 Deweerd, W., 67 DeYoung, J., 232 Dimachkie, W., 108 Doll, O., 361 Dolny, G., 108 Eklund, J., 328 Ellenberger, J., 205 Finstad, C., 86 Foo, T.H., 27 Foster, D., 205 Fransaer, J., 137 Fujita, H., 168 Fyen, W., 392 Gabrielli, C., 320 Gardner, M., 93 Ghekiere, J., 15 Gopalan, S., 93 Goshizono, T., 168 Grant, R., 78 Grebs, T., 108 Grönberg, L., 405 Gross, S., 232 Gunturu, K., 413 Gutt, J., 93 **H**an, W.S., 129 Hartz, C., 205 Hatcher, C., 413 Hatcher, Z., 232 Hattori, T., 222, 289 Hayamizu, N., 168

Electrochemical Society Proceedings Volume 2003-26

Hellin, D., 67 Herring, R., 205

Hess, D., 240, 263 Heyns, M.M., 15, 67, 137, 145 Hoff, A., 378 Holsteyns, F., 145, 161 Hong, C.K., 129 Hou, A., 93 Huff, H.R., 93 Hughes, M., 420 Hunter, J., 123 Ichishima, D., 289 Ikemoto, M., 370 Isti, A., 378 Itou, A., 370 Iyer, S.A., 254 Izumi, A., 34, 57 **J**ohnson, A., 205 Joshi, S., 328 Kashkoush, I., 299 Kenis, K., 145 Kesters, E., 15 Kim, S.Y., 129 Kishimoto, T., 57 Knotter, M., 399 Kolbesen, B.O., 361, 385 Korzenski, M., 222 Kovacs, F., 392 Kraus, H., 67, 392 Kumar, G., 176 Kuniyasu, H., 222, 289 Lappan, R., 413 Lee, B.H., 93 Lee, C.H., 93 Lee, D.-O., 78 Lee, J.-M., 190 Levitin, G., 263 Li, H.J., 93 Loper, S., 116 Louis, D., 355 Lu, Y., 49

Lux, M., 145 Lysaght, P., 93

Ma, C., 232 Madore, M., 355 Maes, A., 161 Mege, S., 320 Mertens, P., 15, 137, 145, 161, 392 Metzger, S., 385 Meuchel, C., 339 Michalowicz, J., 108 Millet, C., 246, 271 Miya, K., 57 Mochizuki, H., 370 Moon, J.T., 129 Moore, J., 339 Morinaga, H., 370 Moumen, N., 100 Mumbauer, P., 78 Munakata, A., 289 Murto, R.W., 93 Muscat, A., 86, 279 Myneni, S., 263 Mytych, J., 108

Naghshineh, S., 305, 420 Nemeth, D., 299 Nguyen, V., 27 Nolan, T., 299 Novak, R., 299

Oborina, E., 378 Okamoto, A., 289 Onsia, B., 67 Ostermann, E., 320

Parashiv, V., 67 Park, J.G., 190, 311 Pehkonen, A., 405 Perrot, H., 320 Perrut, V., 246, 271 Peters, D., 305, 420 Peterson, J., 93

Electrochemical Society Proceedings Volume 2003-26

Philit, G., 355 Prasad, J., 413 Puurunen, R., 67

Raccurt, O., 153 RamachandraRao, V.S., 254 Renault, O., 271 Ridley, R., 108 Rignon, M., 246 Riley, D., 100 Rink, I., 399 Riskin, A., 161 Ritala, H., 195, 405 Rohr, E., 67 Roman, P., 78 Rosato, J., 42, 49 Ruzyllo, J., 78, 108, 347

Saga, K., 222, 289 Saito, H., 289 Sakurai, N., 168 Sano, K.-I., 34 Sehgal, A., 214 Shallenberger, J., 78, 347 Shanmugasundaram, K., 78, 347 Snow, J., 67, 392 Solehmainen, K., 405 Spuller, M., 240 Straight, J., 123

Tardif, F., 153, 246, 271 Toda, M., 1 Tsai, W., 67 Tsang, C.F., 27 Turkot, R.B. Jr., 254

Uryuu, S., 1

Van Doorne, P., 15, 67 Van Elshocht, S., 67 Vehmas, T., 195 Veltens, J., 145 Vereecke, G., 15, 137, 145, 161 Verhaverbeke, S., 23 Vermeyen, K., 392 Vertommen, J., 67 Via, A., 328 Vinckier, C., 137 Von Aswege, L., 355 Vos, R., 137, 145

Wagener, T., 116 Wagner, M., 232 Walker, E., 305 Wang, J., 87 Witters, T., 67 Wolke, K., 355 Wu, C.-T., 108

Xie, B., 279 Xu, C., 222 Xu, K.,137

Yalamanchili, R., 42, 49 Yamanishi, T., 289 You, S.Y., 190 Young, C., 93

Zhang, Q., 27 Zietzoff, P.M., 93

Electrochemical Society Proceedings Volume 2003-26 431

SUBJECT INDEX

Absorption spectrum, 364 acoustic power, 162 acoustic resonance, 182 accoustic wave, 165 activation energy, 51 aerated solutions, 323 aerosol, 289 AES depth profile, 403 AFM, 25 aliphatic alcohols, 286 alumina particles, 313 aluminum, Al - corrosion, 404 - etch, 399 - etch rate, 26 - interconnect, 25 - via, 25 - via etch, 25 anionic surfactant, 200 APM, 146 ARC layer, 259 argon aerosol, 290 acidic-pH alumina, 311 asymmetric stretch, 229 Atomic Layer Deposition, 69, 87 Avests cell, 407

Backside clean, 393 backside damage, 394 benzotriazole, 305, 420 Bernoulli chuck, 393 betaine, 367 bevel clean, 393 bicarbonate, 265 bond pats, 413 bottom radius, 153 Box-Behnken, 117 breakthrough etch, 109

brush scrubber, 139 **BTBAS**, 125 bubble point pressure, 266 bulk line, 155 Calemel electrode, 406 capillary effect, 192 capillary forces, 157 catechol, 362 cathodic potential, 323 cavitation, 119, 147, 168, 188 cavitation bubbles, 119 chelating agent, 273, 370 charge trapping, 98 chemical additive, 224 chemical planarization, 305 chemically amplified resist, 340 chloride media, 327 choline, 362 chromatographic separation, 390 cluster, 348 Co deposition, 372 cobalt, 381 cobalt contamination, 379 colloidal silica slurry, 328 complexing agent, 361, 386 contact angle, 282, 307, 349 contact resistance, 29, 415 CoO, 306, 370 copper, 17,29, 271 - alloyed Al, 405 - cathode, 404 - cation, 321 - CMP, 376 - contamination, 379 - loss, 31 - oxalate complex, 320 - oxide, 32

Electrochemical Society Proceedings Volume 2003-26

- roughness, 32 - sulphate, 325 Coral, 328 corona charging, 381 corrosion inhibitor, 312, 342 co-solvent, 214, 221, 247, 255, 264 cracked photoresist, 357 critical dimensions, 44, 344 critical etching, 49 cryogenic aerosol, 289 cupric oxide, 423 cuprous oxide, 424 cyclic voltammetry, 322 **D**amage, 121 damage mechanism, 187 damage removal, 113 damescene, 254 deaerated solutions, 324 deep UV photoresist, 246 defect control, 211 defoamers, 343 deformable particle, 177 dendrites, 320 dicetone compounds, 272 diffraction pattern, 161 dilute sulphuric acid, 400 dissolved gas, 119, 149 dissolved gas concentration, 173 dissolved oxygen, 59 dissolved silicon, 59 distilled water, 407 DLVO theory, 311 DOT, 207 double-sided scrubber, 191 drag force, 157, 295 dual damscene, 256 DUV resist, 356

Electron diffusion 403 electrostatic double layer, 177 EOT, 67, 93, 100, 392 equilibrium deformation 180 etch rate, 133 expended liquid, 243 expanded solvent,245 extraction mixture, 272

Film drying, 285 film loss, 46 film repair, 286 FinFET, 378 finite element analysis, 182 fluoride, 130 fluorine contamination, 353 fluorocarbon film, 264 Fowler-Nordheim tunneling, 380 Fresnel zone, 163 FTIR, 205, 237, 281

Galvanic cell, 401 GC-MS, 350

Hamaker constant, 312 Hansen solubility parameters, 216 haze, 138 HDMS, 283 Hf deposition, 372 HF dimmers, 53 HF-last process, 93 high-k dielectric, 67, 86, 93 high-pressure cleaning, 215 Hildebrand solubility,247 Hot DI water, 399 HPLC, 387 hydrodynamic removal, 176 hydrophobic surface, 58

Electrochemical Society Proceedings Volume 2003-26

hydrogen peroxide, 388 hydroperoxide anion, 367 hydrogen termination, 125

ILD, 341 i-line resist, 356 ionic impurity, 303 immersion, 118 immersion tests, 406 interface delamination, 257 inter-layer dielectric, 255 ionizable gas, 339 iron contamination, 379 ITRS, 93

JKP model, 179

Laser cleaning, 190 laser scanner, 302 latex sphere equivalent, 196 lift-off mechanism, 200 light point defects, 103, 302, 328 low-k materials, 17, 184, 232, 246, 254, 272, 376 Luggin capillary, 406

Main etch, 109 mass transfer, 50 material loss, 117 megahertz nozzle, 168 megasonic, 30, 44,117, 219 - cleaning, 145, 373 - frequency spectrum, 186 - power, 370 - transducers, 43 membrane pump, 356 MEMS, 184 metal gate, 392 metal particles, 378 microemulsion, 234

micro-PSD, 125 molecular dynamics, 294 multiphase stripping, 250 multiphasic mixture, 276 Nano-particles, 137, 148 nautomers, 364 Nd:Yag laser, 191 NH₃ anneal, 93 nickel contamination, 379 nitrogen aerosol, 290 NMOS transistor, 94 non-aqueous cleaning, 342 non-contact cleaning, 307 nozzle pressure, 292 Open circuit potential, 421 organic - additives, 391 - adsorption, 350 - defect, 309 organosilicate glass, 280, 305 ortho-quinone, 367 Overbeck's approximation, 312 overflow rinse, 356 oxalate anions, 321 oxidation product, 368 oxide loss, 38, 118 oxidizing strength, 351 oxygen/fluorine plasma, 416 ozonated rinse, 303 ozonated water, 100, 123, 301, 405 ozone/HCl ozone clean, 104 Pad module, 417

ad module, 417
particle
lifting, 139
removal, 116
removal efficiency, 145

- rolling, 139 - sliding, 139 - surface concentration, 141 pattern damage, 370 peroxide titration, 363 pH, 316, 322, 390 piezoelectric, 169 plasma ashing, 285 polymer, 130 polymer crust, 257 polysilicon depletion, 392 polysilicon line, 116, 121 porous Silk, 343 post etch residues, 17,25, 271 pressure cycling, 211 probe sliding, 416 process of record, 123, 299, 308 proximity effect, 147 PSL particles, 176 PVD copper, 306

QMS, 205

Rapid Thermal Cleaning, 347 re-adhesion, 371 reflectance spectra, 408 refractive index, 19 repulsive forces, 153, 195 roughness of Cu, 333 roughness of SiC, 333

Sacrificial agent, 367 sacrificial oxidation, 109 SC-1, 100, 116 SC-2, 100 SCCO₂, 214, 222, 240, 254 Schlichting streaming, 161 scrubber clean, 137 self-aligned gate stack, 88 SEM, 18

serpentine resistance, 345 sheet resistance, 407 shock waves, 153 Si etch rate, 105 SiC etch stop, 18 silanol groups, 288 SILC, 381 silica particles, 313 silicon alloyed Al SiLK, 17, 339 SilK dense, 235 SiLK porous, 235 single wafer, 17, 36 Si₃N₄ diffusion barrier, 87 SiOC surface, 376 slurry, 190 soft etch, 110 solution equilibrium, 52 solvatochromic solubility, 248 SOM. 355 sound pressure, 172 space charge, 133 spectroscopic ellipsometry, 18 spin drying, 58 SPM. 355 spray, 40,118 stability experiment, 386 stability of Al₂O₃, 402 storage ambient, 349 storage box, 349 sub-90 nm, 45 surface - aging, 349 - charge, 197 - tension, 241 - termination, 86 surfactant, 164, 232, 370 surfactant layer, 198 surfactant/chelate solution, 374 symmetric stretch, 229

Electrochemical Society Proceedings Volume 2003-26

Ta residues, 395 TaN, 393 TEM, 234 tension gradient dryer, 123 Ti residues, 397 TiN, 392 TPM, 362 TMAH, 362 trench, 108, 341, 359 tungsten, 375 tungsten gate, 129 TXRF, 68

ULK cleaning, 279 ultrasonic cleaning, 168 ultraviolet (UV), 92 UMOSFET, 108 UV/Cl₂, 110 UV/VIS spectroscopy, 361

Van der Waals, 156, 176, 312 via etch, 25 viscous damping, 185 VPD-ICPMS, 358

W

wafer drying, 57 wafer storage, 347 water - degassed, 11 - electrolytic, 10 - hydrogen dissolved, 9 - mark, 60, 306 - ozonated, 7 wetting fluid, 243 WIW uniformity, 54 working electrocde, 421 WTW uniformity, 54

Zeta potential, 178, 197, 313