CHEMICAL VAPOR DEPOSITION OF ZIRCONIUM TIN TITANATE: A DIELECTRIC MATERIAL FOR POTENTIAL MICROELECTRONIC APPLICATIONS

Ebony L. Mays[1, 4], Dennis W. Hess[2], and William S. Rees, Jr.[1, 3, 4]
Departments of Materials Science and Engineering[1], Chemical Engineering[2], Chemistry and Biochemistry[3], and Molecular Design Institute[4], and
Georgia Institute of Technology
Atlanta, Georgia 30332

ABSTRACT

Scaling of integrated circuit (IC) devices for higher speed and storage capacity have prompted a critical need for a material with an increased dielectric constant to replace SiO_2 ($\varepsilon_r = 4$). In this work, a precursor mixture of zirconium tert-butoxide, tin tert-butoxide, and titanium tert-butoxide were used to deposit zirconium tin titanate thin films on silicon substrates. A liquid evaporation system was used to deliver the precursor to a CVD chamber capable of depositing thin films on wafers up to six inches in diameter. Films were deposited at temperatures from 350 °C to 430 °C. Films showed compositions near $(Zr_{0.2}Sn_{0.2}Ti_{0.6})_2O_{4-\delta}$. Preliminary mercury probe measurements have shown dielectric constants from 20-27 without a post deposition anneal.

INTRODUCTION

Decreasing dimensions in integrated circuit (IC) design have driven the need for high dielectric constant (high k) materials to replace the current benchmark, SiO_2 (k ~ 4). For many reasons, particularly integration issues, the replacement of SiO_2 in silicon-based devices is extraordinarily difficult. Recently, Wilk et al. have reviewed the current status and the stringent requirements necessary to replace SiO_2.(1) Although several binary metal oxide, oxynitride, and silicate compounds are being studied as replacement materials, few can meet all of the stringent requirements for high k dielectrics in silicon-based devices.

In an effort to explore properties of new materials systems more quickly, several researchers have used a combinatorial processing approach.(2),(3),(4) In 1998, van Dover et al.(4), used a composition-spread approach to explore the dielectric constant of a wide range of zirconium tin titanate (ZTT) materials. Magnetron sputtering was used to deposit graded ZTT compositions across a substrate. Compositions were mapped across the substrate and electrical properties measured. The sputter-deposited ZTT films had dielectric and electrical properties that were highly dependent on processing conditions such as deposition temperature and percentage O_2 in the sputtering atmosphere. A region of the ternary phase diagram was identified where amorphous films exhibited dielectric constants two to three times larger than those of TaO_x films ($\varepsilon \approx 50$ to 70). Further investigation of this region of the phase diagram revealed an optimum dielectric constant for the composition $(Zr_{0.2}Sn_{0.2}Ti_{0.6})_2O_{4-\delta}$. In addition, the same region showed leakage

currents from 10^{-9} to 10^{-7} A/cm^2 at 1 MV/cm. The properties of this material suggest that it may be a viable high k candidate for CMOS devices.

Chemical Vapor Deposition (CVD) is an attractive technique for the deposition of ZTT films because it offers distinct advantages relative to other deposition methods. CVD is currently used for the deposition of many oxide films in the IC industry, and so is a well-established production technique. In addition, many processing parameters can be controlled and varied in the optimization of the film microstructure and composition.

The possibility of implementing a ternary metal oxide presents an interesting opportunity for the design of CVD precursors. In traditional CVD processing of thin films, a separate metal-organic precursor for each desired cationic film component is fed (i.e., evaporated or bubbled with a carrier gas) into the reactor chamber for reaction at or near the substrate surface. In the case of ZTT, this means that an individual metal-organic precursor for Zr, Sn, and Ti would be needed. The stoichiometry of deposited films is then manipulated through trial and error by altering the relative ratios of the precursor solutions via mass flow controllers; compositional analysis for deposited films then guides subsequent experiments. Indeed, this methodology has proved successful; systematically adjusting stoichiometric ratios and processing parameters establishes a processing window for the desired film properties. However, this procedure is time consuming; the deposition of desired AlGaAs films by this technique took more than a decade to come to fruition. In order to expedite the production of desired ZTT films, our efforts utilize a single ZTT metal-organic precursor solution for the production of ZTT films. This approach requires the introduction of a single precursor solution containing all of the cationic components into the reactor chamber, and thus offers the possibility of improved control of precursor introduction.

EXPERIMENTAL

ZTT thin films were deposited in the CVD reactor shown schematically in Figure 1. The system is capable of delivering precursors with a range of vapor pressures. Precursors with sufficient vapor pressure can be routed from a bubbler at room temperature through a tee directly to the reaction chamber by vapor draw. Precursors with vapor pressures insufficient for vapor draw are introduced to the reaction chamber via direct liquid injection (DLI). The precursor (at room temperature) is pushed from a bubbler to a vaporizer. The vaporizer transforms the liquid to a vapor/mist at elevated temperature. Vapor is then delivered to the chamber by He push gas through an injection ring. The injection ring uniformly disperses the precursor in the chamber above the wafer. As shown, a deflector plate is used to direct the precursor or precursor mixture to the wafer while baffling the flow of oxygen delivered from the top of the chamber. To optimize the delivery of precursor to the wafer surface, the injection ring and deflector plate are held in place by compression fittings, which allows the ring and plate to be positioned at varying heights above the wafer. All tubing/connections after the vaporizer are heated with heating tape to approximately 105 ºC and the chamber walls are heated to approximately 70 ºC to prevent precursor condensation. The heated platen upon which substrates were placed is 6 inches in diameter.

A solution of zirconium tert-butoxide, tin tert-butoxide, and titanium tert-butoxide, formulated by Schumacher Inc., was used to deposit ZTT thin films. Preliminary work investigating this and other precursors for deposition of ZTT was reported by Senzaki et al.(5) Because of the low vapor pressure of the precursor mixture, it was delivered to the reaction chamber via the DLI system. The composition of the solution was prepared to correspond to the desired composition of the final film; for our studies, this required a Zr:Sn:Ti molar ratio of 1:1:5 for the composition $Zr_{0.2}Sn_{0.2}Ti_{0.6}O_x$. In this way, the precursor solution may be tailored for optimum compositional and electrical characteristics.

A series of films were deposited on 4-inch p-type Si(100) substrates ($\rho < 0.1$ Ω-cm) at substrate temperatures of 350 °C, 370 °C, 390 °C, and 430 °C. Immediately prior to deposition, the silicon wafers were cleaned in a 50:1 H_2O:HF solution for 15 seconds and then positioned on the platen. Wafers were introduced into the chamber through a glove bag under nitrogen flow. The wafer was then heated to the deposition temperature. The wafer and vaporizer temperatures were allowed to stabilize for 10 minutes before precursor was delivered to the chamber. Each deposition was performed at a chamber pressure of 3 Torr in an oxygen flow of 100 sccm, a precursor flow of 0.06 ml/min, and He carrier flow of 200 sccm for 11 minutes.

Film thickness was measured using a Woollam Variable Angle Spectroscopic Ellipsometer (VASE) with spectral range from 193 nm to 1700 nm. Measurements were taken at angles of 65º, 70 º, and 75º. X-ray Photoelectron Spectroscopy (XPS) was performed using a PHI 1600/3057 with a standard aluminum x-ray source. Rutherford Backscattering (RBS) was performed at the Arizona State University iBEAM facility using a 1.7MV Tandetron (tandem ion accelerator) made by General Ionex. Capacitance analysis was conducted at Schumacher Inc., using an MDC mercury probe MP200.

RESULTS/DISCUSSION

Ellipsometry

Ellipsometry measurements were performed in a matrix of 9 points on each wafer. The thickness was determined at each point and the individual measurements averaged to obtain the reported film thickness. Table I summarizes the kinetic data. Figure 2 shows a plot of the ZTT film thickness on Si(100) substrates as a function of substrate temperature. The ZTT film thickness increases with increasing substrate temperature. A maximum growth rate of 105 Å/min was achieved at 430 ºC. Figure 3 shows an Arrhenius plot of the ZTT growth rates versus 1/T for both sets of wafers. The trend shows two of the three characteristic regimes often reported in thin film growth by CVD.(6) In the growth regime, encompassing 350 ºC to 390 ºC, growth increases rapidly, nearly exponentially. Growth is typically limited by reaction at the surface. The activation energy for film growth, calculated from the slope of the exponential growth region, is 42.9 kcal/mol. The measured activation energy compares well with activation energies reported in previous work for deposition of ZrO_2 films using zirconium tert-butoxide alone. Cameron et al. have discussed the CVD of ZrO_2 thin films from two manufacturers of zirconium tert-butoxide. Activation energies of 27±8 kcal/mol and

30±6 kcal/mol were reported. These activation energies were attributed to β-hydride elimination of t-butoxy surface species and were compared to values of E_a = 38-45 kcal/mol for the β-hydride elimination of ethyl groups on Si(111)7X7 and E_a= 49±6 kcal/mol for β-hydride elimination of ethyl and ethoxy groups on Si(100)2X1.(7) Burleson et al. have also described the growth kinetics of CVD-deposited ZrO_2 films using zirconium tert-butoxide citing similar results.(6) The activation energy for deposition of ZTT films is intermediate between the two cited authors because in both cases deposition was performed using zirconium tert-butoxide alone. In our case, the precursor solution also contains tin tert-butoxide and titanium tert-butoxide whose interactions may change the growth kinetics. Additionally, Cameron et al. used water as the oxidant while Burleson et al. used no additional oxygen source for deposition of ZrO_2 films. In our case, additional oxygen was supplied to the chamber during deposition that likely changes the growth mechanism compared to the references cited.

The second growth regime encompassing the temperatures between 390 ºC and 430 ºC shows a plateau in the growth rate. This regime is limited by reactant flux to the surface. Depending on the sticking coefficient of reactant species, all reactant reaching the surface has the capacity to react. In this regime, increasing the flow of reactant increases the deposition rate. Although higher deposition temperatures cannot be achieved with the current equipment, depositions at temperatures above 430 ºC should show a decrease in growth rates characteristic of transport-limited growth.

X-ray Photoelectron Spectroscopy and Rutherford Backscattering Analysis

XPS was used to conduct compositional analysis on all films. Table II summarizes the compositions of the ZTT films. Carbon levels were below the detection limit of XPS analysis after a 60 second Ar sputter to remove adventitious carbon. Although film compositions reside in the desired region ($Zr_{0.2}Sn_{0.2}Ti_{0.6}O_x$), no correlation between composition and deposition temperature can currently be made.

An important property of any replacement material for SiO_2 is a low leakage current under the operating field. Unfortunately, many transition metals typically have more than one stable oxidation state, as is the case for TiO_2. The high dielectric constant, ~ 80-110 depending on morphology and processing conditions (1), make it an attractive candidate for the replacement of SiO_2. But pure TiO_2 is known to have mixed oxidation states of Ti3+ and Ti4+ that cause high leakage currents in capacitors fabricated from this material. Similarly tin oxide is known to have oxidation states of Sn2+ (stannous) and Sn4+(stannic). Thus, control of film oxidation will be important in the optimization of the material properties of ZTT films. For each film, the XPS Ti2p peak was investigated at high resolution to determine whether a shoulder was present indicating the existence of more than one oxidation state. Gaussian simulations of the Ti2p peaks were compared to the experimentally measured shape. The areas of the two Gaussian peaks were then used to determine the percentage of Ti4+ and Ti3+ oxidation states present in the films. For all films, the percentage of Ti4+ predominated over the percentage of Ti3+ present, but none of the films were fully oxidized despite the presence of oxygen in the precursor ligands and the addition of oxygen to the chamber during deposition. As shown in Table II, the films deposited at 350 ºC and 370 ºC were the most fully oxidized but there is no trend in the degree of oxidation with temperature.

RBS analysis was performed on films of adequate thickness; Table III summarizes the film compositions. Although the compositions compare well with those determined using XPS, RBS data indicate that the film deposited at 430 °C exhibited a composition gradient. Analysis showed a surface layer and a sub layer of comparable thickness with significantly differing compositions. The ellispometrically determined thickness was used to calculate a density of 4.33 g/cm^3 for the film deposited at 390 °C. This can be compared to a density of 5.0 g/cm^3 (8) and 5.1 g/cm^3 (9) for crystalline ZTT with orthorhombic crystal structure of composition $Zr_{0.8}Sn_{0.2}TiO_4$ produced using traditional powder processing.

AFM Analysis

Atomic Force Microscopy was used to measure the surface roughness of a 10x10µm area of each film. All films exhibited roughness between 0.8 to 2.2 nm and no pits were observed.

Mercury Probe Capacitance Analysis

Mercury Probe capacitance analysis was conducted on all wafers at 10^5 Hz. No measurement was possible for the film deposited at 350 °C, as the leakage across the film was too high. This was due to the fact that the film was very thin (< 10 nm) and was subjected a high electric field. Measurements of the films deposited at 370 °C, 390 °C, and 430 °C yielded dielectric constants that ranged from 20 to 27. The variation in k values observed was presumably due to differences in leakage current, i.e. thickness for a specified electric field. The dielectric constants achieved compare well with those of Senzaki et al. (k ~ 20-30) using the same and/or similar precursor solution and similar final ZTT composition. But the achieved dielectric constants in both cases were 50% or more less than those achieved by van Dover et al. (k ~ 50-70) which were measured at 1 kHz.(4),(10),(11)

CONCLUSION

ZTT thin films in the range of $Zr_{0.2}Sn_{0.2}Ti_{0.6}O_x$ can be deposited by CVD from a solution of zirconium tert-butoxide, tin tert-butoxide, and titanium tert-butoxide using a heated-wall reactor. A maximum deposition rate of 105.3 Å/min was achieved. Ellipsometric measurements showed an exponential increase in growth rate for deposition temperatures in the range between 350 °C and 390 °C. Above 390 °C the growth rate shows a plateau. Composition of the ZTT thin films varied with deposition temperature, but no trend between deposition temperature and composition was apparent. XPS analysis of Ti2p peaks showed that all films had mixed Ti oxidation states. The films deposited at 350 ° C and 370 ° C were most fully oxidized, but no correlation could be made between deposition temperature and degree of oxidation. Preliminary mercury probe analysis of films showed dielectric constants from 20 to 27.

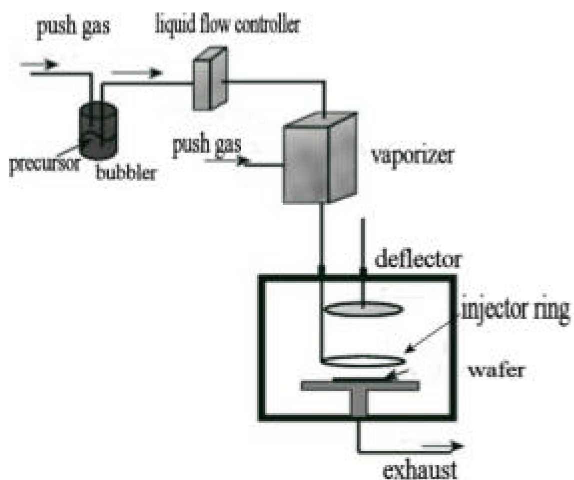

Table I. Summary of Kinetic Data

Temp, °C	Thickness, nm	Rate, nm/min
350	9.4	0.9
370	27.7	2.5
390	75.9	6.9
430	115.8	10.5

Figure 1. Illustration of reactor.

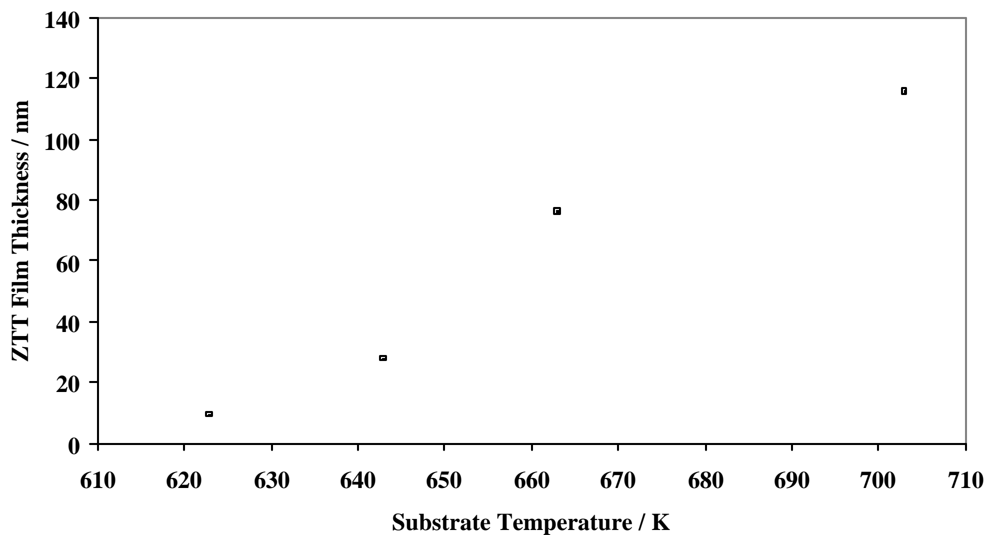

Figure 2. ZTT film thickness versus substrate temperature.

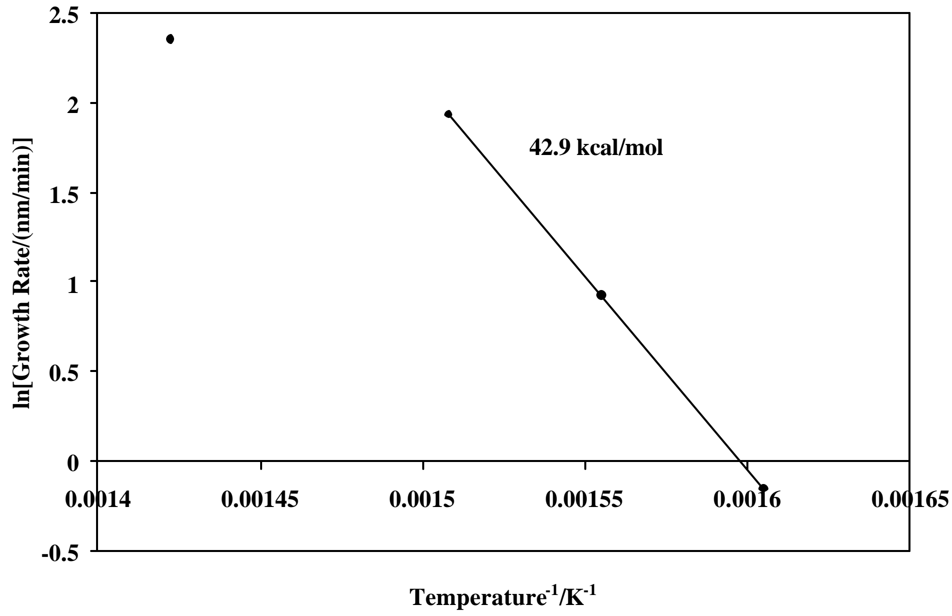

Figure 3. Arrhenius plot of ZTT growth rate versus 1/T.

Table II. Summary of XPS Data

Temp, ºC	**Composition (Atomic Concentration)**				**Ti^{4+}/Ti^{3+} %Area of Ti2p peak**
	O1s	**Ti2p**	**Zr3d**	**Sn3d**	
350	68.61	6.92	16.91	7.55	97.86/2.14
370	65.85	5.75	18.46	9.94	94.40/5.6
390	67.84	17.47	10.10	4.59	60.51/39.49
430	68.06	20.85	5.65	5.45	80.23/19.77

Table III. Summary of RBS data

Temp, ºC	**Composition (Atomic Concentration)**				**Thickness Areal density ($Atoms/cm^2$)**
	O	**Ti**	**Zr**	**Sn**	
390 ºC	67	15	12	6	$5.50x10^{17}$
430 ºC	68	21	6	5	$4.57x10^{17}$
	70	15	9	6	$4.70x10^{17}$

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