Investigation of copper removal efficiency on reclaimed wafers with HF-based solutions

A.Abbadie(1), P.Besson(2), S. Favier(2), C.Giroud(3), and M.N.Séméria(3)
(1) **PICOPOLISH France**, CD 56, route des Michels, 13790 PEYNIER.
(2) **STMicroelectronics**, 850, rue Jean Monnet, 38921 Crolles, France.
(3) **CEA-LETI**, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.

Introduction

The prevention of metallic contamination is an important issue in the semiconductor industry because of its harmfull impact on devices. Particularly, eliminating Cu contaminants is essential to preserve the materials integrity. It is all the more important when wafers are repetitively processed in a reclaim industry. Then, Cu must be efficiently removed from the wafers' back-sides and front-sides to avoid any cross-contamination. Dilute HF solutions are most commonly used to remove metallic contaminants [1]. However, copper deposition is influenced by the pH and the redox-potential of the solution [2]. We have thus explored the effect of reagents such as HCl and oxidant additives such as H_2O_2 on copper removal. We have concentrated on the efficiency of these cleanings and on the surface morphology after treatment. We show that for our application, additives in the HF solution of the SC_2/HF/SC_2 cleaning do not improve the surface morphology. On the contrary, they underline an heterogeneous surface topographic aspect.

Experimental

We have used <100> oriented, 200mm diameter reclaimed wafers with a 3 layers stack, as described in fig.1. SC_2 1/2/5- 5% HF- SC_2 1/2/5 sequences were used to remove copper from contaminated wafers (back-side and front-side). The first SC_2 ($HCl/H_2O_2/H_2O$) sequence allows Cu layer and TiN barrier removal from the wafers front-side. The 5% HF solution (for 5 min) is used for etching of the chemical oxide on the front-side. Finally, the last SC2 sequence at 70°C is designed to remove Cu from the back-side. We have used for the two SC2 sequences a dipping time of 5 min, at a temperature of 70°C and with a 1/2/5 concentration. We have then compared the efficiency of 4 etch chemistries based on the addition of reagents in the HF solution:

- HCl 1% and 5%
- H_2O_2 1% and 5%

The Cu contamination level was measured by Vapor Phase Decomposition-Absorption Atomic Spectrometry (VPD-AAS). Tapping mode Atomic Force Microscopy (AFM) was used for the inspection of surface roughness and morphology. The surface morphology after cleaning was inspected using Scanning Electron Microscopy, and supplemented by an EDX analysis (Energy Dispersive X-Ray) to confirm Cu elimination from the wafers' front-side.

Results-Discussion

1° Copper elimination from the wafer's back side: As shown in figure 1, both chemistries using HCl as a reagent in the HF solution of the SC_2 + HF sequence reduce the amount of Cu on the back-side to final surface concentrations between 10^{10} and 10^{11} at/cm^2 (same efficiency as HF alone). Whatever its concentration, the addition of a high oxidant species such as H_2O_2 reduces the metallic contamination level to values below the LLD (Low Level of Detection). So, due to its electrochemical properties, the presence of H_2O_2 in the HF solution contributes to efficiently clean Copper contaminated wafers [3]. The last SC2 sequence is enough to achieve after 5 min a Cu contamination below the LLD whatever the nature of the additive.

2° Surface roughness: The AFM measurements after each etch chemistry based on the SC_2/HF/SC_2 cleaning are reported in figure 2 for two AFM scanning field sizes (1µm and 2µm). The presence of HCl or H_2O_2 in the HF solution induces a surface roughening with a Rmax increase (observed especially with HCl). These additives can favorize the copper complexation, due to the presence of O_2, OH^- and Cl^-. The AFM images plotted fig. 4 and 5 reveal topographic variations on the surface and the presence of clusters or adsorbates. This heterogeneous aspect is observed with both additives, HCl or H_2O_2, and seems to increase when the concentration of these reagents is higher.

3° Surface topography: This surface morphology was obtained as well after a SC_2/HF/SC_2 cleaning (fig 6-1) without any additive, with a lower density of adsorbates, however. With 5% HCl or H_2O_2, about the same topography is observed (fig.6-2 and 6-3). However, an analysis by EDX and SEM showed a Cu contamination below the LLD, besides a slight C and O contamination. The clusters are suspected to be metallic impurities, particles or silicides due to room-temperature Cu out-diffusion. [4].

Conclusion

A SC_2/HF/SC_2 cleaning has enabled us to obtain Si reclaimed wafers with a copper contamination significantly reduced (front-side and back-side). Neverthless, without or with additives such as HCl or H_2O_2 in the HF solution, the same heterogeneous Si surface topography is obtained, responsible for a high rms roughness. The addition of reagents is thus not beneficial in terms of surface morphology after reclaim.

References

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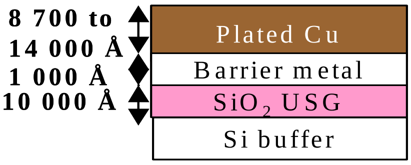

Fig.1 Layer stack of the tested wafers

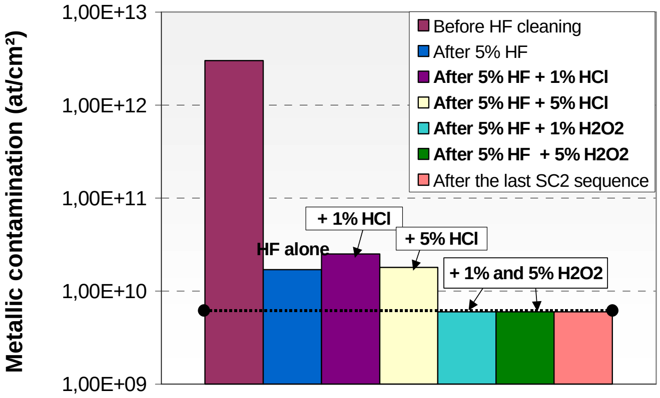

Fig. 2: Copper removal efficiency on the wafer's back-side analysed by VPD-ICPMS as a function of the reagent (HCl or H_2O_2) in the HF solution of the SC_2/HF/SC_2 cleaning.

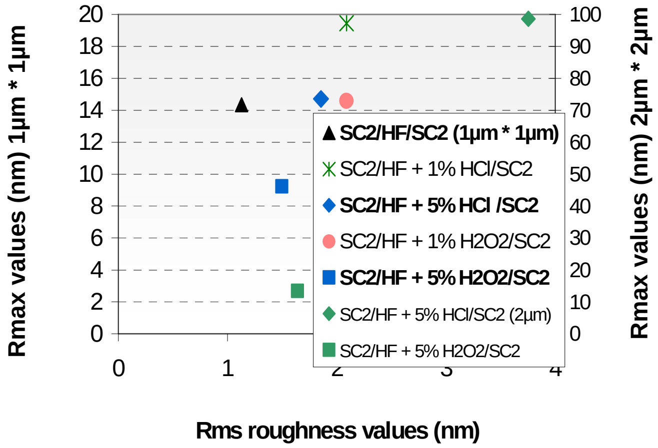

Fig. 3. Rms roughness and Rmax values (in nm) obtained by tapping-mode AFM for the different conditions of treatment in the SC_2/5% HF/SC_2 sequence.

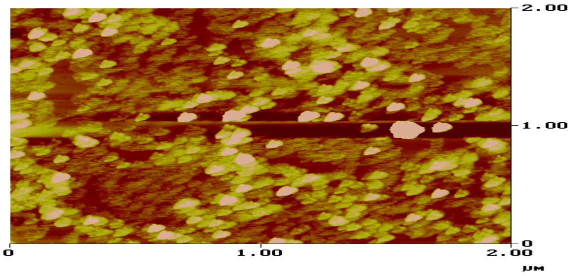

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Fig.4. AFM (2µm × 2µm) image after a SC_2/5% HF + 5% HCl/SC_2 cleaning sequence.

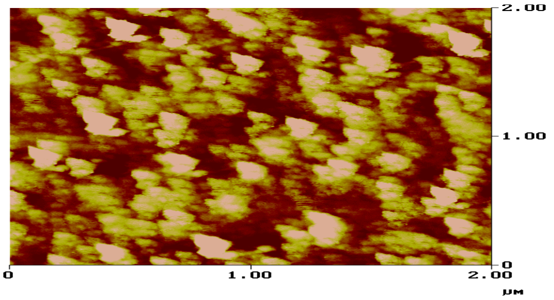

Fig.5. AFM (2µm × 2µm) image after a SC_2/5% HF + 5% H_2O_2/SC_2 cleaning sequence.

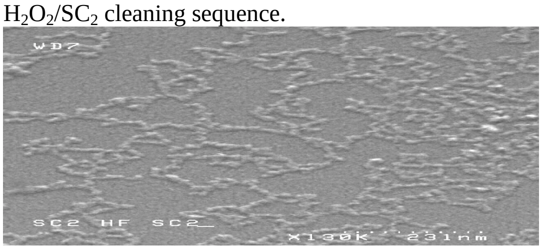

Fig.6-1. SEM image of the Si surface after a reclaim by the SC_2/5%HF/SC_2 sequence.

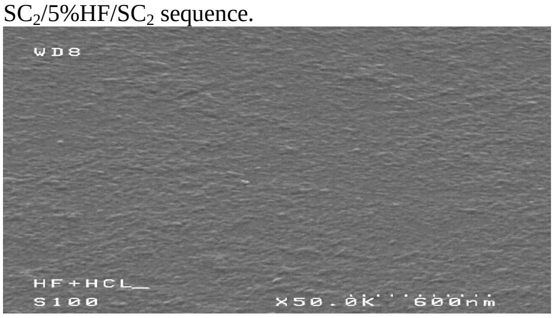

Fig.6-2. SEM image of the Si surface after a reclaim by the SC_2/5%HF + 5% HCl/SC_2 sequence.

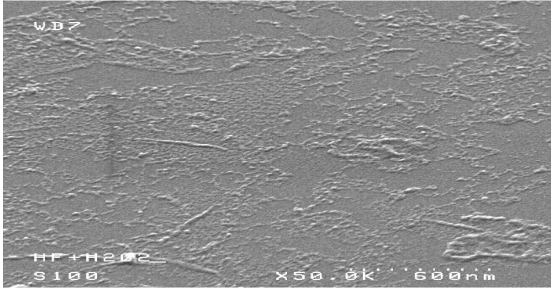

Fig.6-3. SEM image of the Si surface after a reclaim by the SC_2/5%HF + 5% H_2O_2/SC_2 sequence.

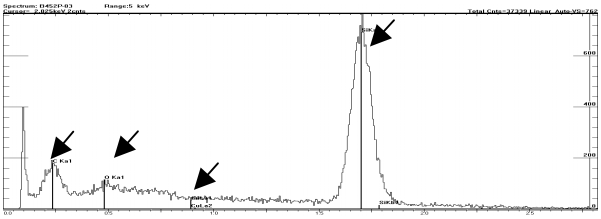

Fig.7. EDX spectrum obtained after a SC_2/5% HF + 5% HCl/SC_2 treatment. The arrows from left to right represent the contamination: C, O, Cu and the Si peak