Mechanism of metal ions adsorption on PVA brush during post-CMP cleaning

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INTRODUCTION

Chemical mechanical polishing (CMP) is a critical process for the global planarization of various surfaces in semiconductor manufacturing, especially as technology progresses to smaller than 10 nm nodes [1-4]. Meeting the stringent requirements for CMP and minimizing defects, especially particle count, has been of great interest to the overall success of the CMP process. Particles remaining on the wafer surface after CMP can get embedded into the surface, blocking subsequent photolithography and leading to pinholes in the deposited film [5]. Among several types of post-CMP cleaning processes, polyvinyl acetal (PVA) brush cleaning has been the most effective method for contaminant removal due to the physical force imposed by direct contact between the brush and wafer surface that also provides a low cost of ownership (COO) [6-8]. The dominant removal forces during brush scrubbing are the contact elastic force, hydrodynamic drag force, and friction between brush and particles. In the boundary lubrication regime, particles can be removed by rolling and lifting, mainly due to van der Waals forces [8-11]. The development of novel and advanced post-CMP cleaning techniques is required to remove different types of contaminants effectively (e.g. particulate, organic, metallic, *etc.*) from surfaces. One of the issues during post-CMP processes is that the contaminants can be easily transported to the brush to cause cross-contamination of the wafers and decrease the brush lifetime. Unlike oxide CMP, metal CMP leaves metal ions, which can pass over post-CMP and contaminate the brush, which causes contamination and scratches on the surface [12]. The PVA brush could be severely contaminated by metal~~lic~~ ions in the form of complex or converted metal~~lic~~ oxides which can recontaminate the wafer while reusing the brush for metal post-CMP cleaning. Hence, it is required to understand the metal ion contamination of the brush during post-CMP cleaning and to study the metal ion-brush interaction mechanism.

BACKGROUND

Metal ion removal is very critical to consider in STI post-CMP cleaning. It is postulated that metal ions or complexes are firmly attached to the PVA brush surface by coordinative or covalent bonding. Post-CMP cleaning of metal ions can impact the overall yield of the CMP process. The defect generated in the post-CMP cleaning process can also lead to complications in subsequent fabrication processes. Metal ions such as copper ions are generated during CMP and post-CMP cleaning processes because of the chemical etching of the substrate. The accumulation of metal ions inside the PVA brush was studied using a dipping and scrubbing experiment. Even after rising, a significant amount of copper ions was seen to be present inside the brush as detected by inductively coupled plasma mass spectrometry (ICP-MS) analysis, which confirmed the possible chemical or physical interaction between the metal ions and the PVA brush. In our previous discussions, we studied the brushes with different metal~~lic~~ ions (Cu, Ti, W, and Co) to understand the metal-brush bonding nature and various conditioning methods to remove metallic contaminations.

EXPERIMENTAL

The interaction between the brush and copper ions was studied using the dipping experiment where, the brush nodules of approximately 3 mm were cut from a commercial 200 mm PVA brush (AION Co. Ltd., Japan), followed by dipping in standard copper ions solution (ICP-MS standard) with two different concentrations, 100/1000 ppm at three pH conditions (3, 7, and 11). The schematic representation of the experimental procedure for contamination, conditioning, and rinsing methods is illustrated in Figures 1 and 2. The dipped samples were rinsed with the DIW. The morphology of contamination in the brush nodules was examined using FE-SEM analysis (FE-SEM, S4700, Hitachi). To observe the level of copper ions on brush loading after dipping, the digestion of brush nodules using H_2SO_4 and HNO_3 (3:2) was performed. The concentration of copper ions in ppm was estimated using ICP-AES (ICP-AES, Spectro Arcos) analysis.

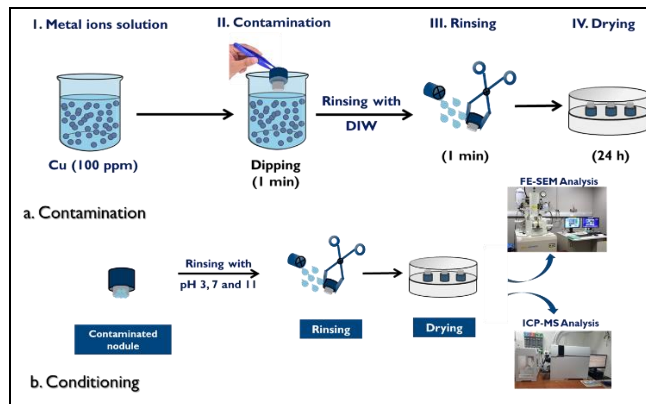


Fig. 1 Experimental procedure for brush contamination and conditioning

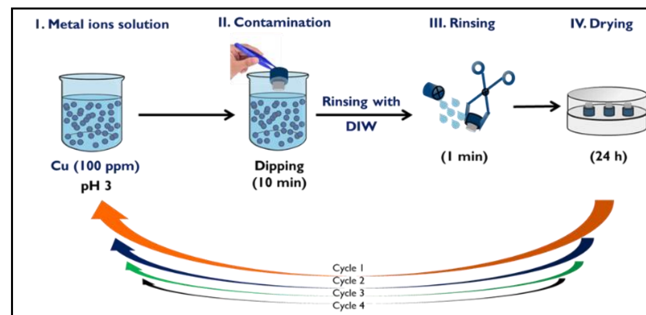
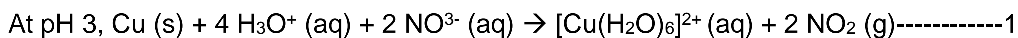


Fig. 2 Experimental procedure to study the effect of dipping and to rinse on the same brush

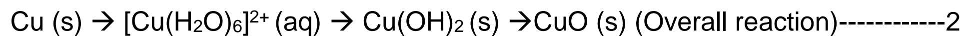
DISCUSSION

1. Effect of Cu ion on brush loading at different pH conditions

The brush nodules were dipped inside the solution containing 100 or 1000 ppm copper ion concentration at different pHs (3, 7, and 11). At the acidic condition (pH = 3), the free Cu^{2+} ions and OH groups from the PVA brush interacted strongly, leading to a strong penetration. The aqueous copper complex, $[Cu(H_2O)_6]^{2+}$ was highly stable (equation 1), and adsorption took place easily.



$$\text{At pH 3, } Cu\ (s) + 4\ H_3O^{+}\ (aq) + 2\ NO^{3-}\ (aq) \rightarrow [Cu(H_2O)_6]^{2+}\ (aq) + 2\ NO_2\ (g) \text{------------1}$$



$$Cu\ (s) \rightarrow [Cu(H_2O)_6]^{2+}\ (aq) \rightarrow Cu(OH)_2\ (s) \rightarrow CuO\ (s)\ \text{(Overall reaction)------------2}$$

By altering the pH from 3 to 7, the OH anion replaced the water and led to the formation of $Cu(OH)_2$. By increasing the OH concentration, $Cu(OH)_2$ converted completely to CuO or CuO_2. Through the FE-SEM image, the particles could be observed on the surface of the brush at pH 7 and 11 but not at pH 3. Interestingly, ICP results showed higher contamination at pH 7 followed by pH 3 and 11. However, because of the poor stability of copper ions at pH 7 and 11, we will stick with pH 3 as the better condition for the Cu ion contamination.

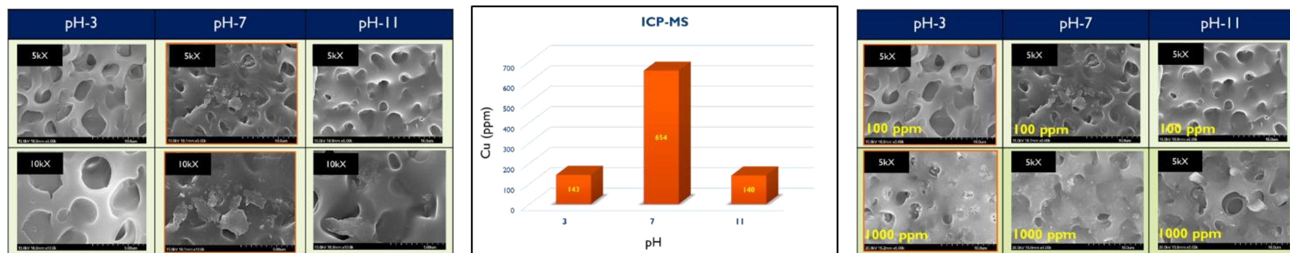
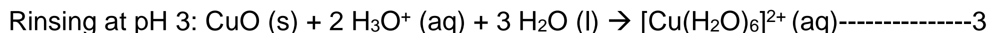


Fig. 3 Brush loading by dipping in Cu ions solution at various pH and ICP-MS analysis of Cu contaminated nodule

2. Effective conditioning method of removal of Cu ions

On rinsing the contaminated nodule with DIW, we selected pH 3 over pH 7 and 11. Interestingly, by rinsing the contaminated nodule with different pH solutions (3, 7 and 11), we deduced that rinsing with pH 3 solution broke

the CuO into [$Cu(H_2O)_6$], which was readily soluble in the water. As shown in equation 3, the hydronium ions were reactive with the CuO particles and dissolved completely. However, in the case of pH 7 and 11, the copper ion concentration was reduced though particles were still observed in the FE-SEM images (Figure 4). Similarly, ICP results also follow the same trend.


Rinsing at pH 3: $CuO\ (s) + 2\ H_3O^+\ (aq) + 3\ H_2O\ (l) \rightarrow [Cu(H_2O)_6]^{2+}\ (aq)$---------------3

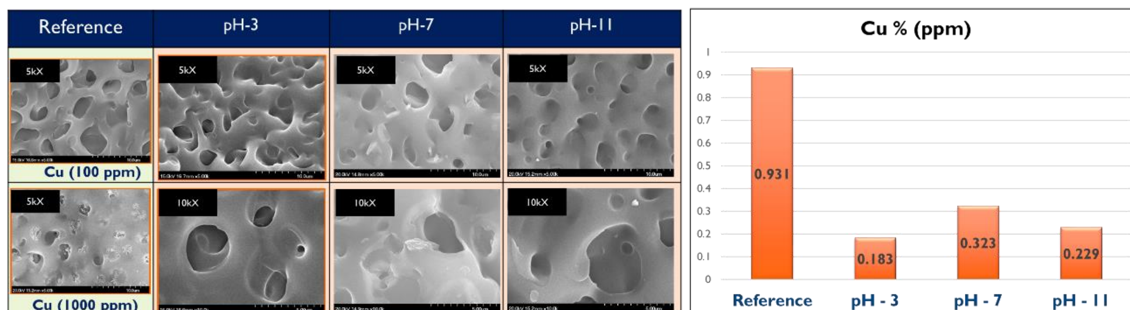


Fig. 4 FESEM and ICP-AES of brush rinsed at various pH

3. Effect of dipping and rinsing on the same PVA brush

This experiment aims to find the saturation level of Cu contamination in the PVA brush after five cycles. The brush nodules were dipped for 10 minutes, rinsed with DIW for 1 minute, and analyzed the samples. The experiment was repeated in the same contaminated nodule to check the maximum loading under different cycles. We observed that after 1st cycle, copper ions converted into $Cu(OH)_2$ and CuO particles *via* aggregation. The Cu ion concentration gradually increased up to the 3rd cycle, fell from the 4th cycle, and saturated. Both FE-SEM and ICP results were very much helpful in understanding the fundamental chemistry (Figure 5).

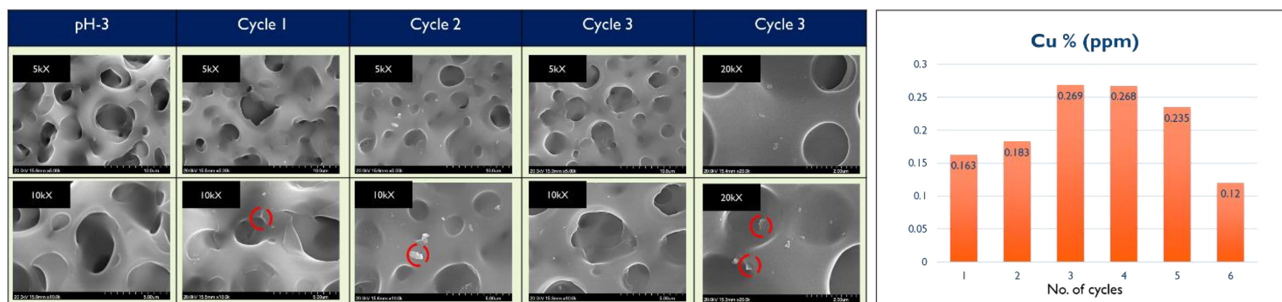


Fig. 5 FESEM and ICP-AES of brush dipped at pH 3 and rinsed with DIW at repeated cycles

CONCLUSION

In our study, we discussed the level of contamination of Cu ions and its interaction with the PVA brush. Contamination and conditioning experiments were analyzed using FE-SEM and ICP-MS/AES techniques. The Cu loading was stable at pH 3 compared to pH 7 and 11 conditions. Rinsing the contaminated samples with pH 3 solution effectively removes Cu contaminants by forming a soluble aqua complex, whereas rinsing with pH 7 and 11 regenerated the particles. Also, we have discussed the maximum loading of Cu ions in the single nodules by repeating the dipping and rinsing for five cycles, which revealed the saturation after the fourth cycle. Still, many experiments are ongoing to complete the objective of our work.

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