Analysis of Corrosion Inhibitor Effects in Cu CMP Based on AFM Measurements

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ABSTRACT

During copper CMP process, corrosion inhibitor plays a key role for preventing corrosion and attaining global flatness on the wafer surface. To improve CMP performance, it is very important to establish the correlation between the passivation layer characteristics and inhibition performance. In this study, an investigation of material characteristics with an intentional AFM scratch / FD curve was conducted for analyzing the effect of corrosion inhibitor and the passivation layer in Cu CMP. The mechanical analysis of passivation layer was carried out with AFM FD curve measurements. The relationship between energy dissipation, scratch depth, deformation, adhesion force and Material Removal Rate / Static Etch Rate was investigated and established. Finally, passivation layer will decrease the concentration of nano-scale defect / scratch will decrease, which is meaningful that this result will lead to the overall yield improvement and nano-scale defect reduction of the CMP process.

1. INTRODUCTION

Chemical Mechanical Planarization (CMP) is widely conducted to achieve global planarization of wafer surfaces during semiconductor integrated circuit (IC) manufacturing. Currently, the importance of CMP gradually increases, while design rule and device sizes decrease. CMP also used for manufacturing the copper (Cu) interconnects, which are widely used for integrated circuit fabrication. Cu is commonly widely used as an interconnecting material due to is outstanding properties, as high electrical and thermal conductivities, high electro-migration resistance, and low cost [1,2]. However, even Cu with such excellent material properties has a fatal disadvantage that corrosion occurs easily. If corrosion occurs, there is a defect in the Cu surface, which leads to deterioration of the performance of the device. Therefore, to prevent corrosion of Cu, which has an adverse effect on device performance and yield, a corrosion inhibitor is added to the slurry to proceed with the CMP process.

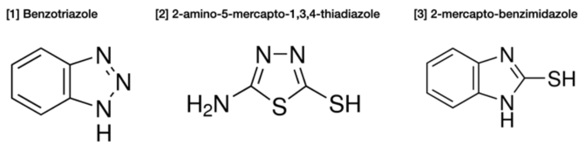


Figure 1. Molecular structures of corrosion inhibitors

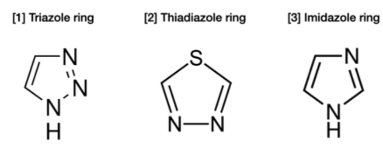


Figure 2. Molecular structures of azole group rings

Cu CMP slurry consists of many ingredients as abrasive, oxidant, inhibition agent, complex agent, pH adjustor to achieve global planarization [3]. During the Cu CMP, a passivation layer is generated on the Cu surface. Then, the passivation layer is polished by slurry abrasive such as silica particle. The chelating agent blocks re-adsorption of Cu complex residues which are detached from the wafer surface during the Cu CMP. Corrosion inhibitors are essential for obtaining global planarization in wafer surfaces and preventing corrosion during Cu CMP. The oxidizer creates Cu ions by oxidizing the Cu surface [4,5]. The Cu ions combine with the complexing agent to form a Cu complex [6-8]. Corrosion inhibitors reduce the corrosion reaction in the trench at the wafer pattern, enabling global and local planarization [9-11].

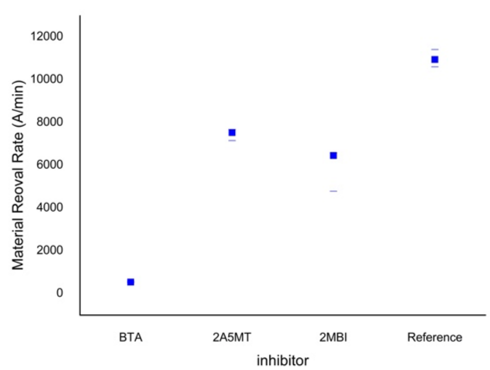
Nonetheless, research about analysis of chemical / electrical / mechanical characteristics of passivation layer according to inhibitor characteristics and CMP material removal rate (MRR) / corrosion control is still insufficient. Therefore, in this study, unlike conventional corrosion inhibitors that analyze inhibition performance by analyzing the electrical properties of Cu surfaces (i.e., Potentio-dynamic polarization, Nyquist plot), various Atomic Force Microscopy (AFM) measurements were analyzed. Finally, we analyzed material characteristics of passivation layer based on AFM measurements.

2. EXPERIMENTAL

The Cu wafer was layered with Ti 500 Å / Cu 7000 Å and was a 4cm x 4cm size Coupon wafer. The thickness measurement of the Cu wafer was performed with 4-point probe CMT-SR5000 (AIT). The slurry formulation consists of DIW 466.67 g, abrasive [EXP351] 16.67 g, complex agent [glycine] [98 %] 5 g, pH adjuster [HNO_3] 0.1M 1 ml, oxidant [H_2O_2] 30 wt% 16.67 g, inhibitor agent 0.25 g (1) Benzotriazole (BTA) (2) 2-amino-5-mercapto-1,3,4-thiadiazole (2A5MT) (3) 2-mercapto-benzimidazole (2MBI) (4) Reference. The CMP experiment was conducted by POLI-400L police (G&P TECH) and HD-319B pad (SKC). Wafer pressure is set to 210 g/cm^2 and the speeds of heads and platen are set to 87 RPM and 93 RPM, respectively. The polishing time is 60 seconds, and the slurry flow rate is set to 120 mL/min. To accurately understand the corrosion inhibition efficiency of each inhibitor, the static etch rate (SER) was measured excluding the influence of abrasives. The slurry used in the SER was tested by replacing the abrasive with DIW, measuring the thickness of the 4 cm X 4 cm Cu wafer first, and then measuring the thickness of the Cu wafer after being immerged in the slurry solution prepared for 1 minute to calculate the SER as the thickness difference between the two thickness values. Next, various investigations of passivation layer were conducted by AFM. To analyze the material properties of the Cu passivation film, adhesion force, scratch depth, energy dissipation, and deformation were measured by AFM NX-10 (Park Systems), NSC-36 / 3M cantilever.

3. RESULTS AND DISCUSSION

As shown in Figure1, 3 types of corrosion inhibitor (1) benzotriazole (2) 2-amino-5-mercapto-1,3,4-thiadiazole (3) 2-mercapto-benzimidazole were evaluated. Figure 2 indicates the azole group ring structure of the corrosion inhibitors used. Each inhibitor consists of heterocyclic compounds containing azole groups such as triazole, thiadiazole, and imidazole.



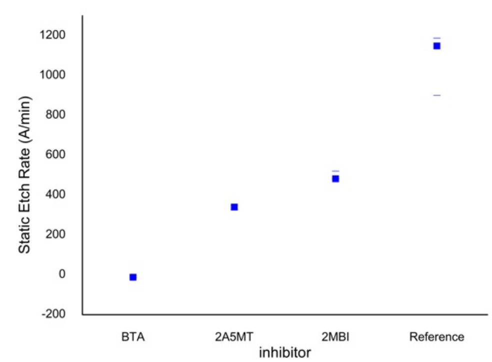


Figure 3. Cu CMP MRR of corrosion inhibitors

Figure 4. SER of corrosion inhibitors

As shown in Figure 3 and 4, corrosion inhibitors inhibition effect of corrosion inhibitors was investigated. According to the AFM FD curve measurement, the inhibited area indicates lower adhesion force, energy dissipation, and higher deformation. Based on those mechanical properties, it is possible to determine whether inhibitor is adsorbed, relative hardness of passivation layer, and maximum surface energy capacity. As shown in Figure 5 and 6, we found that the adhesion force / energy dissipation / deformation all increased in the order of BTA, 2A5MT, 2MBI, and reference with the similar tendency as the MRR / SER. Also, Figure 7 indicates that the AFM scratch depth showed the same tendency as MRR results. The Scratch depth is inversely proportional to the inhibitor's inhibition performance, suggesting that the inhibition efficiency can also be mechanically analyzed. Based on scratch depth / MRR results, it was confirmed that inhibition not only chemically protects corrosion but also protects Cu surface from mechanical external force such as scratch and polishing. This result suggests that the passivated wafer surface can be protected from scratches and nano scale defects that occur during the CMP process. So, further work is being pursued to improve the yield and investigate the Post Cu-CMP cleaning mechanism by advanced AFM measurements.

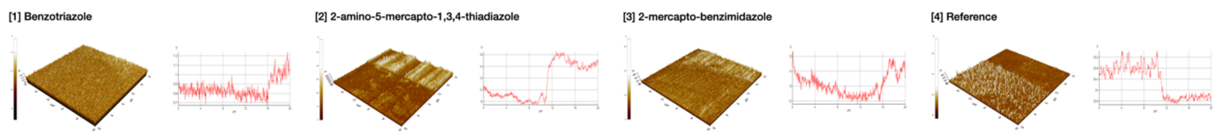


Figure 5. Energy dissipation of passivated surface (Left) and bare Cu wafer surface (Right)

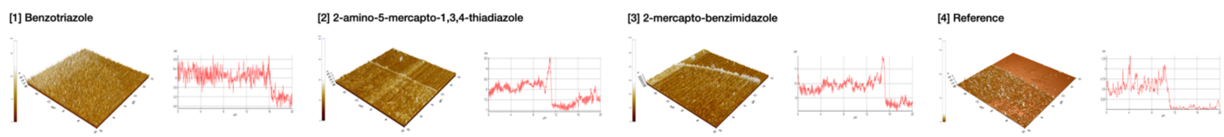


Figure 6. Deformation of passivated surface (Left) and bare Cu wafer surface (Right)

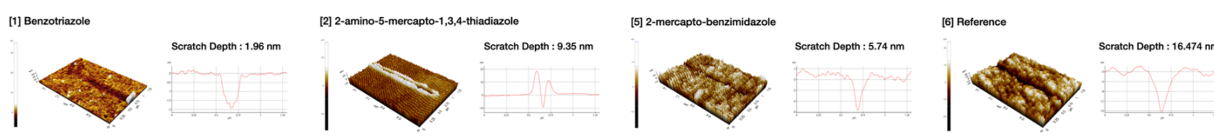


Figure 7. AFM Scratch depth of passivated Cu surface

4. CONCLUSION

Finally, in this paper, the effect of the inhibitor used to prevent the corrosion of Cu surface was verified. The material properties of the passivation layer were analyzed through AFM FD curve measurement. The correlation between Cu-inhibitor complex characteristics and MRR / SER was established by comparing the tendency between AFM measurement results and MRR / SER results. We found that the more effective the corrosion inhibition occurs, the smaller adhesion force / energy dispersion / scratch depth / deformation becomes. Based on the prior correlation, we propose that the passivation layer can protect the scratches and the nano-scale defects that occur during the CMP process. As a follow-up study, we will conduct a more advanced mechanical / electrical / chemical characteristics analysis of passivation layer to establish a correlation between passivation layer characteristics and CMP / Cu CMP Cleaning performance, which will achieve yield improvement and Post Cu CMP cleaning mechanism.

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