

Effect of Glycerol on Cu-CMP and Investigation of its Mechanism by Novel Dynamic LSV System

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Abstract

Chemical mechanical polishing (CMP) slurries consist of numerous ingredients with unique properties, and polyol is one of them. Glycerol seems particularly interesting because of the presence of three neighboring hydroxyl groups that may exhibit a strong interaction with abrasives or metal lines. However, the mechanism of such additives has always remained uncertain, because typical analysis such as linear sweep voltammetry (LSV) is conducted under static conditions whereas CMP involves a mechanical process. In this report, therefore, the effect of glycerol toward CMP was first examined. Then, the novel dynamic LSV system was employed to further investigate how this polyol compound worked in the Cu-CMP slurry. Our result indicated that glycerol was effective to reduce dishing, and that it worked via the adsorption to Cu surface.

Introduction

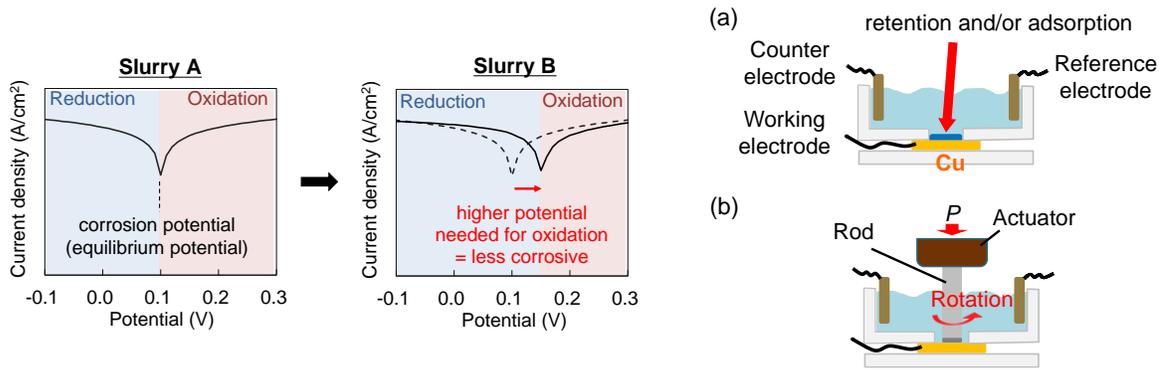
Chemical mechanical polishing (CMP) has become an essential technology in semiconductor industry since its birth. As the size of semiconductor chips shrinks, small defects that was once allowed is becoming no longer acceptable. There are numerous factors that affect surface conditions, but slurry compositions play a significant role among them.

Metal-CMP slurries typically consist of abrasive, oxidizing agent, and chelating agent. Also, corrosion inhibitor is of considerable importance in order to prevent excessive oxidation toward metal lines. In copper CMP (Cu-CMP), benzotriazole (BTA) is one of the most widely used inhibitors. It is known to be quite effective yet often undesired, because it forms insoluble Cu-BTA complex that requires extensive post-CMP washing [1,2]. Therefore, its alternatives have been searched for many years. Polyols are attractive candidates in this regard. They are known to interact with other elements via hydroxyl groups, so that they may adsorb to wafer and/or abrasive and form a protective coating while being highly soluble in water. 1,2,3-propanetriol, commonly known as glycerol, is particularly appealing among such compounds. It has three neighboring hydroxyl groups that may exhibit a strong interaction with other elements. If glycerol can bind to the abrasives, for example, it will affect the particle size distribution, and/or zeta potential. On the other hand, if it forms a protective coating on metal surface just like BTA, surface defects such as dishing may be reduced.

Linear sweep voltammetry (LSV) is a powerful electrochemical technique in which one can evaluate the corrosion potential of metal as shown in Figure 1. However, the corrosion tendency measured by LSV does not always correspond to the one observed in actual CMP process. This is because the electrochemical reaction generates a concentration gradient of slurry as well as retention of metal oxides near the electrode's surface as shown in Figure 2(a), which disturbs the subsequent oxidation, whereas such layer is readily removed by polishing pad in CMP. Nevertheless, there is no apparatus commercially available that enables the dynamic electrochemical analysis, so it has always remained uncertain that how slurry additives work in the actual CMP process.

Therefore, *Doi Laboratory Inc.* recently developed "d-EC", a dynamic LSV system. It consists of not only the electrodes and voltammetry cell, but also a polishing rod and actuator component (Figure 2(b)). This system allows one to obtain a voltammogram (also known as Tafel plot) while rubbing the metal surface just like the CMP process. If glycerol's adsorption is weak, then the plots of dynamic LSV should look the same regardless of with or without it, because it will easily be removed by polishing rod. On the other hand, if its adsorption is strong enough, it should keep sticking to copper and affect the corrosion.

In this research, therefore, we investigated the effect of glycerol toward surface roughness in Cu-CMP, and conducted dynamic LSV in order to explore its mechanism.



(Left) Fig. 1 Examples of Tafel plot

(Right) Fig. 2 Diagrams of LSV instrument: (a) typical apparatus (b) dynamic apparatus

EXPERIMENTAL

CMP experiment

CMP experiments were performed by bench-top polishing machine ML-160 (*Maruto Instrument*) with IC1000 XY-perforated pad (*Nitta DuPont*). Blank slurry was prepared by mixing 1% colloidal silica (average particle size: 125 nm), 6.1% citric acid, and 0.4% hydrogen peroxide [3]. The second and third slurries (*BTA* and *GLY*, respectively) were prepared by adding 0.24% of BTA or glycerol to the blank. The fourth slurry (*BTA+GLY*) contained both 0.24% BTA and 0.24% glycerol. pH of these four slurries were 1.6, 1.6, 1.6, 1.7, respectively. CMP experiments were conducted by using a 18mm×18mm piece of Cu-spattered pattern wafer (Cu thickness approx. 750nm) with the pressure of 5.89 psi at 60 rpm while the slurry was provided at 12 mL/min. The polishing time for *Blank*, *BTA*, *GLY*, and *BTA+GLY* were 10 min, 53 min, 11 min, and 53 min, respectively. After Cu layer was removed, surface roughness was measured by atomic force microscopy (AFM) on 1 μ m/1 μ m line/space pattern for three times, slightly moving the target spot for each scan. The depth of dishing was reported as the average of the three runs.

LSV experiment

All electrochemical measurements were conducted by using the dynamic LSV system “d-EC” (*Doi Laboratory Inc.*). The appearance of d-EC is shown in Figure 3. A piece of wafer with Cu film (1.5 μ m thickness) was employed as working electrode. For the static measurement, the rod and actuator were kept uplifted. After the slurries without silica were poured into the cell, voltammograms were run from -2.00 V to +2.00 V with 0.01 V increment, and 0.5 s interval at each data point. For the dynamic measurement, the rod with bottom area of 1 cm² was lowered and pressed onto the working electrode until 40 g of weight (0.6 psi) was applied. Then, voltammograms were run with the same parameters as the static condition after the actuator was turned on at 40 rpm.

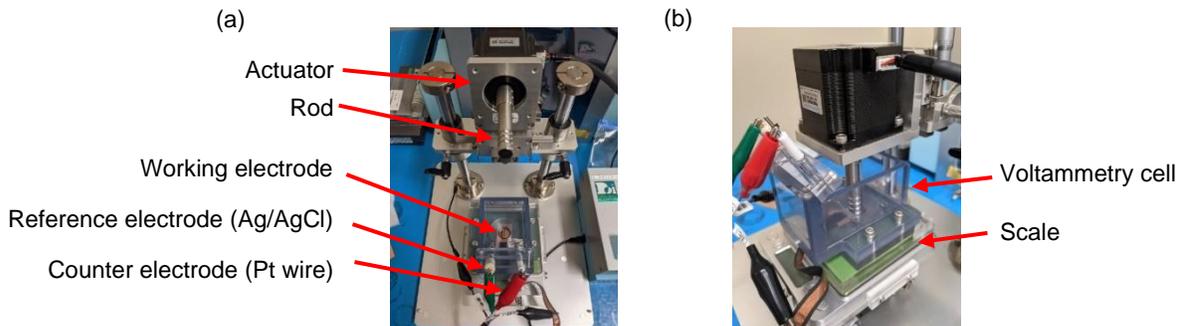
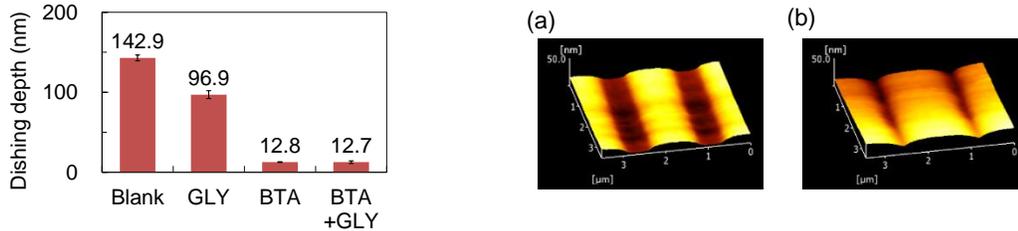


Fig. 3 Appearance of d-EC: (a) front view (rod/actuator uplifted) (b) side view (rod/actuator lowered)

Result and DISCUSSION

The effect of glycerol on the depth of dishing is shown in Figure 4. Dishing was reduced from 142.9 nm to 96.9 nm when glycerol was added. This means that it is a mildly effective additive. Just as expected, however, it was far less powerful than BTA, which caused only 12.8 nm of dishing. Thus, the use of glycerol along with BTA may seem pointless at first glance as the difference in dishing depth was only 0.1 nm. Nevertheless, a combination of BTA and glycerol (*BTA+GLY*) exhibited a significant improvement on the surface condition as shown in Figure 5.



(Left) Fig. 4 Effect of slurry additives on dishing

(Right) Fig. 5 AFM images of 1 μ m/1 μ m line/space pattern: (a) BTA (b) BTA+GLY

There are two possibilities regarding how glycerol reduced the damage to Cu line; adsorption on abrasive, or that on copper. As shown in Figure 6(a), the zeta potential of *GLY* was slightly higher than that of *Blank*. Therefore, glycerol might have adsorbed to the colloidal silica and induced the repulsion of abrasives, which mildly affected the polishing rate and the surface condition. However, the zeta-potentials of *BTA* and *BTA+GLY* were approximately the same as *GLY*, whereas their polishing rates and dishing depth were quite different from it. Therefore, the zeta-potential (or the interaction between silica and glycerol) was probably not the major reason why glycerol reduced the dishing. We also investigated the particle size distribution of the slurries. As you can see in Figure 6(b), however, the distributions showed no shift by adding glycerol and/or BTA. On the basis of these data, it is unlikely that the improvement on dishing depth was caused by the adsorption of glycerol to the colloidal silica.

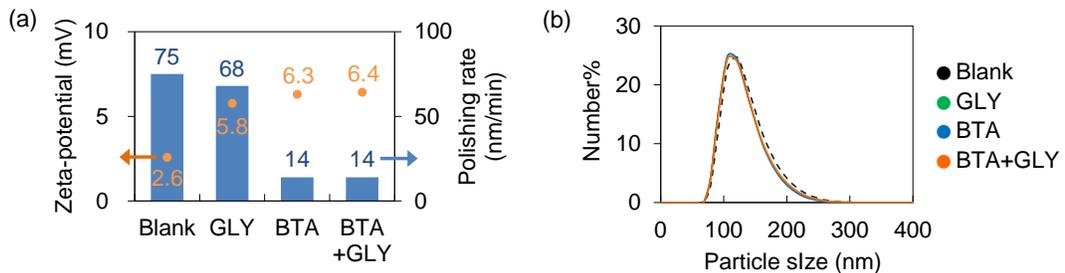


Fig. 6 Properties of slurry: (a) Zeta-potential and polishing rate (b) particle size distribution

The other possibility is glycerol's adsorption on copper surface. Tafel plot of the four slurries are shown in Figure 7. The corrosion potentials in the static LSV were as follows: *Blank* (0.07 V) < *GLY* (0.13 V) < *BTA* (0.17 V) < *BTA+GLY* (0.20 V). The higher the corrosion potential is, the less corrosive the slurry. Therefore, the electrochemical analysis appeared to be consistent with the CMP experiment. This result suggests that glycerol worked as corrosion inhibitor toward copper, and it enhanced the effect of BTA when they were added together.

However, as discussed in the previous section, the static LSV is not quite conclusive yet because it is affected by the condition near the surface of working electrode. Therefore, we proceeded to the dynamic measurement, and then, *GLY* inhibited corrosion more than *Blank*, and similarly so did *BTA+GLY* than *BTA*. (Figure 7; bold lines and red arrows). Thus, it can be finally said that the surface roughness was improved in the CMP experiment as a result of glycerol being adsorbed on the copper surface with such a strength that it could not be easily peeled off.

Notably, *BTA* and *BTA+GLY* became more corrosive when switched to the dynamic measurements as shown in blue or orange arrow. This makes sense because the dynamic system removed the solution retained near the copper surface and let the fresh metal be exposed, which promoted the

oxidation reaction. However, the change in the corrosion potentials was quite small for these two solutions. This suggests that the Cu-BTA complex strongly retained on Cu surface so that the polishing was barely effective to accelerate the oxidation. On the other hand, the plots of *Blank* and *GLY* shifted to the right when the dynamic system was employed, indicating that metal corrosion was suppressed as opposed to *BTA* or *BTA+GLY* (Figure 7; black and green arrow). This shift was, however, unexpected. There is a possibility that the absence of strong corrosion inhibitors like BTA somehow affected the dynamic measurement, but we cannot propose any reasonable explanation at this point. Thus, more detailed investigations on the effect of slurry compositions are needed.

Furthermore, the fact that *BTA+GLY* further improved the surface condition whereas glycerol was only mildly effective by itself suggests that the combination of glycerol and BTA was critical. In other words, glycerol works more effectively when it is present with Cu-BTA complex. This is quite reasonable because glycerol and BTA can be expected to interact through hydrogen bonding. The plausible images of glycerol working as corrosion inhibitor is shown in Figure 8. Negatively charged oxygen atoms in the hydroxyl groups of glycerol can bind to copper atoms regardless of the presence of BTA. However, when BTA is present, they can form the additional hydrogen bonding to the nitrogen atoms. The extra corrosion inhibition in *BTA+GLY* can be explained by these interactions.

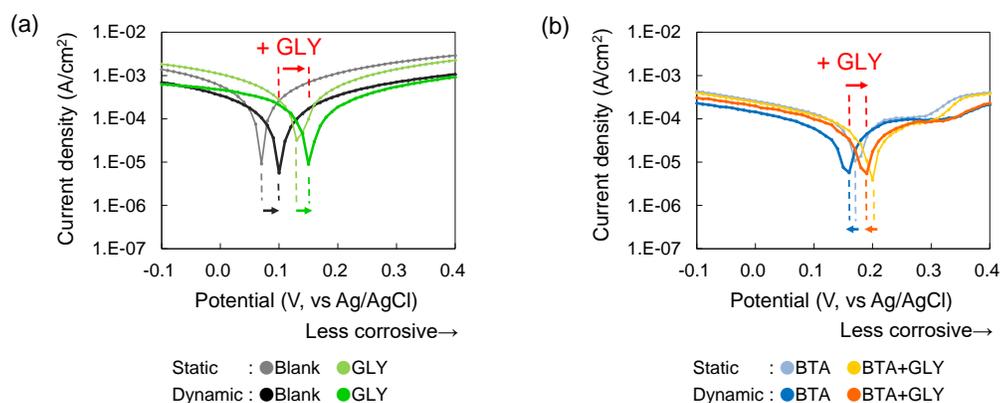


Fig. 7 Tafel plot of static and dynamic LSV measurement: (a) *Blank* & *GLY* (b) *BTA* & *BTA+GLY*

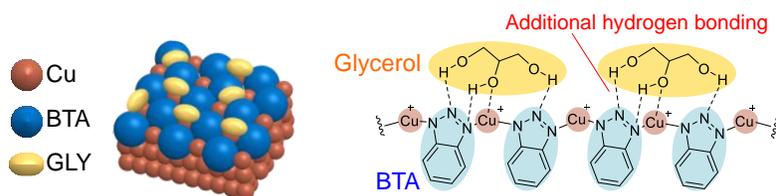


Fig. 8 Plausible mechanisms of glycerol's adsorption on Cu-BTA complex

CONCLUSIONS

The effect of glycerol in Cu-CMP slurry was studied, and its adsorption behavior was investigated by the novel dynamic LSV system. We observed the reduction in dishing when glycerol was added to the slurry, and notably, the combination of BTA and glycerol turned out to be even more effective. Also, we were able to reveal the mechanism with the help of dynamic LSV that glycerol inhibited corrosion by adsorbing to the copper surface. On the basis of these results, we would like to continue our research on the mechanism of CMP technology.

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