A Rotating Ring Disk Study of Accelerators with Cl^- and Br^- for Copper Damascene Electrodeposition

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The acceleration effects of bis (sodiumsulfopropyl) disulfide (SPS) and its derivatives in the presence of Cl^- and Br^- were studied using a rotating ring disk electrode (RRDE) in a $\text{CuSO}_4/\text{H}_2\text{SO}_4$ solution. The positive ring current increased with the addition of accelerators providing that the Cu(I) thiolate complex was formed during the dissolution step of electrodeposition. SPS and mercaptopropylsulfonic acid (MPS) show better acceleration effect with Cl^- while propane-1,3-disulfonic acid (PDSH) has higher acceleration effect with Br^- . The highest acceleration effect is achieved with 4 ppm of PDSH and 50 ppm of Br^- . Copper electrodeposition, which was conducted using periodic pulse reverse current waveform with $I_{\text{on}} = -20 \text{ mA/cm}^2$, achieved perfect filling with 2 ppm of PDSH and 50 ppm of Cl^- in which the ring currents measured at dissolution step are significant. Results show that the cuprous complexes which formed during the dissolution step hastened via-filling.

Keywords : Copper Electrodeposition, Acceleration, Additives, PDSH, Rotating Ring-Disk Electrode

1. Introduction

The electrodeposition of copper for on-chip metallization is involved in the manufacturing of semiconductor devices. This is called the Damascene process, and the trenches and vias are then filled by copper electrodeposition. The electrodeposition process of filling trenches and vias depends on the additives. The additives produce bottom-up filling and achieve a void-free filling of the trenches and vias.¹⁾ Recent studies have focused on the acceleration effect of accelerators such as SPS, MPS and Cl^- .²⁾⁻⁴⁾ Moffat and West proposed a curvature-enhanced mathematical model in which the accelerators are assumed to be adsorbed at the curvature and accelerates electrodeposition of copper on via bottoms.^{2),3)} The importance of interaction between SPS and Cl^- was described by Dow.^{4),5)} However, Moffat curvature enhanced model, in principle, does not refer to two step copper reduction reaction.

On the other hand, there have been lots of experimental evidences which indicate that the formation of cuprous intermediate during the electrodeposition process.^{6),7)} K. Kondo formed experimentally verified the relation between the cuprous ions and acceleration effect by using the trench bottom electrodes. The results showed that the current densities increased for the narrower trench. The current densities with N_2 bubbling were larger than that with O_2 bubbling. The differences in current densities must be caused by the accumulation of Cu(I) thiolate complex at the bottom.⁸⁾ E. E. Farndon proposed the following reactions among SPS, Cl^- and cupric ion.^{9),10)}

M. Tan experimentally proved that SPS derivative without thiol group also shows acceleration effect with the presence of Cl^- .¹¹⁾ Recently, K. Kondo accumulated experimental and theoretical work on SPS - Cl^- acceleration. A cuprous intermediate model has been proposed that involves the formation of Cu(I) thiolate complex at the bottom of the via.¹²⁾ T. Hayashi measured the increases in cuprous ion production with SPS and Cl^- additives using a RRDE. Negative ring current density rose with the addition of SPS and Cl^- .¹³⁾

In this report, the cuprous complexes concentration was monitored during the dissolution of copper on disk electrode by RRDE to determine the acceleration effect of accelerators in the presence of halogen ions Cl^- and Br^- . While the interactions between SPS or MPS and Cl^- have been reported in many studies, PDSH has not been received much attention although it has analogous structure with SPS, contains two sulfonate group, no thiols group. M. Tan demonstrated that the acceleration effect came from the interaction between sulfonate group and chloride ion.¹¹⁾ Therefore, we decided to investigate and optimize the acceleration effects of PDSH by various electrochemical measurements. Furthermore, electrodeposition of vias was also conducted using these accelerators to compare with electrochemical measurements.

PDSH was prepared and supplied by Tosoh Finechem Corporation.

2. Experiment

Linear Sweep Voltammetry (LSV) was undertaken using a RRDE. The working and counter electrodes are platinum and the reference electrode is a saturated calomel electrode (SCE). The basic bath consisted of 200 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 25 g/L H_2SO_4 . The additives were SPS, MPS, PDSH, Cl^- and Br^- . The rotation speed was kept at 1000 rpm. Prior to measurement, the bath was bubbled with N_2 for 1 hour. Temperature of the bath was kept at 25 °C.

To measure amount of cuprous produced, the ring potential was set at +0.5 V. The copper electrodeposition was performed for 45 seconds at -0.3 V to produce copper thin film on disk electrode. After preprocessing, the disk potential shifted from 0 to 0.5 V vs. SCE under a potential sweep rate 15 mV/s.

For the via-filling, a periodic reverse pulse current waveform was applied, with $I_{\text{on}} = -20 \text{ mA/cm}^2$, $I_{\text{rev}} = 60 \text{ mA/cm}^2$, $I_{\text{off}} = 0 \text{ mA/cm}^2$ and $T_{\text{on}} : T_{\text{rev}} : T_{\text{off}} = 200 : 10 : 100 \text{ ms}$. The via samples consisted a polyimide thin film laminated with copper foil. The via holes with 50 μm diameter were formed by photolithography. These via samples were attached to rotating disk electrode and rotated at 500 rpm. The electrodeposition time is 45 minute. The filled via samples were examined by observing their cross sections. The cross sections were formed by initially polishing with emery paper and then 1.0 μm particle diameter Al_2O_3 as the final polishing step. The filled via cross section was observed by optical microscopy.

3. Result

Fig. 1 indicates the ring current at positive ring potential with chloride and bromide as additive alone. X-axis is the disk potential and y-axis is the ring current. (a), (b), (c) are the ring currents with 10 ppm, 50 ppm and 90 ppm of chloride. (d), (e), (f) are the ring currents with 10 ppm, 50 ppm and 90 ppm of bromide. (g) is the ring current of basic bath. The ring current increased drastically with the presence of chloride and bromide ions. In addition, the ring currents with bromide were larger than that of chloride. The ring current increased gradually with the increase of chloride concentration and reached the highest at 90 ppm of chloride. At 0.42 V, the ring current with 90 ppm of chloride is twofold higher than basic bath. For bromide, from 10 ppm to 50 ppm, the ring current increased gradually it decreased when the concentration

Fig. 1 Comparison of acceleration effect of chloride and bromide at different concentrations.

of bromide was higher. In brief, chloride and bromide showed their acceleration effects and bromide potentially has higher acceleration effect than chloride.

Fig. 2 indicates the ring current at positive ring potential with various concentrations of SPS in the presence of chloride and bromide ions. X-axis is the disk potential and y-axis is the ring current. (a), (b), (c) are the ring currents with 1 ppm, 2 ppm and 4 ppm of SPS in the presence of chloride. (d), (e), (f) are the ring currents with 1 ppm, 2 ppm and 4 ppm of SPS in the presence of bromide. (g) is the ring current of basic bath. With the presence of chloride, the ring current increased in the range of 1 ppm and 2 ppm of SPS then decreases at 4 ppm. The ring current with 2 ppm of SPS and 50 ppm of chloride is the highest, that means, the amount of Cu(I) thiolate formed at dissolution step are largest. With the presence of bromide, the ring current decreases with the increased of SPS concentration from 1 ppm to 4 ppm. The ring current with 4 ppm of SPS is only one third of the ring current with 1 ppm of SPS and 50 ppm of bromide. In brief, chloride ion shows better acceleration effect together with SPS although bromide ion shows stronger acceleration effect when it is used alone.

Fig. 3 indicates the ring current at positive ring potential with various concentrations of MPS in the presence of chloride and bromide ions. X-axis is the disk potential and y-axis is the ring current. (a), (b) are the ring currents with 2 and 4 ppm of MPS in the presence of chloride. (c), (d) are the ring currents with 2 and 4 ppm of MPS in the presence of bromide. (e) is the ring current of basic bath. The ring current with 50 ppm of chloride and 4 ppm of MPS is the highest that means the total amount of cuprous ions formed at dissolution step is largest. The ring current with MPS and bromide was slightly smaller than MPS and chloride. With the presence of bromide, the ring currents did not show much different. The ring current with MPS and bromide decreased with the increase of MPS concentration from 2 ppm to 4 ppm.

Fig. 4 indicates the ring current at positive ring potential with various concentrations of PDSH in the presence of chloride and bromide ions. X-axis is the disk potential and y-axis is the ring current. (a), (b), (c) are the ring currents with 1 ppm, 2 ppm and 4 ppm of PDSH in the presence of chloride. (d), (e), (f) are the ring currents with 1 ppm, 2 ppm and 4 ppm of PDSH in the presence of bromide. (g) is the ring current of basic bath. There was a small increase in ring current when PDSH concentration

Fig. 2 Ring current at various concentrations of SPS in the presence of chloride and bromide.

increases. With the presence of bromide, the ring current with 4 ppm of PDSH is the highest, 0.75 mA at 0.4 V. In general, the ring currents with PDSH and bromide are higher than that of PDSH and chloride. At 0.25 V, the ring current with PDSH and bromide is 1.5 times larger than PDSH and chloride. Therefore, the Cu(I)-complex concentration or acceleration effect of PDSH in the presence of bromide is higher than that in chloride.

Fig. 5 shows the peak of ring currents at different concentration of accelerators SPS, MPS and PDSH from 1 to 6 ppm in the presence of chloride and bromide at 0.4 V of disk potential vs. SCE. It can be easily seen that the ring currents of PDSH with chloride and bromide are higher than that of MPS and SPS. That means PDSH potentially has better acceleration effect with chloride and bromide than MPS, SPS. This difference with PDSH must be due to the two sulfonate groups, without thiol end groups as in MPS and SPS.¹¹⁾ The trends of relation between accelerators concentration and ring currents are also indicated clearly in the figure. For example, the ring current with bromide and SPS increased from 1 to 2 ppm of SPS then dropped rapidly with further increase in SPS concentration. The ring currents are proportional to the amount of cuprous complex formed at dissolution step. Therefore, we can choose the optimum concentration of each accelerator with bromide and chloride for copper electrodeposition by comparing the ring currents.

Fig. 3 Ring current at various concentrations of MPS in the presence of chloride and bromide.

Fig. 4 Ring current at various concentrations of PDSH in the presence of chloride and bromide.

Fig. 6 shows the optical micrographs of cross sections of vias filled using different accelerators with chloride and bromide. A periodic reverse pulse current waveform was applied, with $I_{on} = -20 \text{ mA/cm}^2$, $I_{rev} = 60 \text{ mA/cm}^2$, $I_{off} = 0 \text{ mA/cm}^2$ and $T_{on} : T_{rev} : T_{off} = 200 : 10 : 100 \text{ ms}$. The basic bath consist of CuSO_4 and H_2SO_4 , the additives are Cl^- 50 ppm, PDSH 2 ppm, PEG 25 ppm and SDDACC 10 ppm for (a) and Br^- 50 ppm, SPS 4 ppm, PEG 25 ppm and SDDACC 10 ppm for (b). From the micrographs, (a) was perfect filled without voids but via (b) has the voids at the center. The results are predictable because the ring current of Br^- 50 ppm and SPS 4 ppm is only 0.23 mA, one-third to the ring current of Cl^- 50 ppm and PDSH 2 ppm from **Fig. 5**. Therefore, we can conclude that the cuprous complex formed at dissolution process accelerated the electrodeposition.

4. Conclusion

1. Bromide as alone additive has higher acceleration effect than chloride. The optimum concentrations of chloride and bromide are 90 ppm and 50 ppm, respectively.
2. The ring current increases with the increase of SPS concentration in the presence of chloride. For bromide, the ring current decreases when SPS is added. Therefore, SPS reduces effectively to MPS with chloride than bromide.
3. The ring currents increase with the addition of MPS to both solution containing chloride and bromide. The acceleration effect with MPS and chloride is slightly higher than MPS and bromide. The highest acceleration effect is MPS 4 ppm and

Fig. 5 Comparison of ring currents at different concentration of accelerators with the presence of chloride 50 ppm and bromide 50 ppm at 0.4 V disk potential vs. SCE.

Fig. 6 Cross sectional views of via holes. (a) Cl^- 50 ppm, PDSH 2 ppm, PEG 25 ppm and SDDACC 10 ppm, (b) Br^- 50 ppm, SPS 4 ppm, PEG 25 ppm and SDDACC 10 ppm.

chloride 50 ppm.

4. The acceleration effect of PDSH with bromide is higher than that with chloride. In the presence of bromide, the ring currents do not change much with the increase of PDSH concentration. The highest acceleration effect is with PDSH 4 ppm and bromide 50 ppm.
5. PDSH does have promising acceleration effect in copper electrodeposition. Via-fillings using accelerator PDSH achieved perfect filled without voids.
6. The electrochemical measurements and via-filling results have strengthened the role of cuprous with bottom up filling mechanism. The more cuprous complex formed at dissolution process, the more acceleration achieved.

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