Mass-transfer Effect of Janus Green B on Copper Elecrtrodeposition in Submicrometer Trenches

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Copper electrodeposition is recently used in the Damascene process for the fabrication of interconnections of ultra large-scale integrated semiconductor devices. To accomplish “superfilling”, which means the successful, void-free filling of copper in submicrometer trenches by electrodepositon, several kinds of additives such as chloride ions (Cl^-), polyethylene glycol (PEG), bis(3-sulfopropyl)disulfide (SPS) and Janus Green B (JGB) are included in the plating bath. It has been reported that SPS added with Cl^- and PEG brings about the “bottom-up” growth, in which the deposition from the bottom of trenches was accelerated, and the bottom-up growth leads to the void-free filling.[1] JGB is regarded as a leveling agent flattening the bumps of deposits on the surface or influences the filling properties. However, the behaviors of JGB, particularly in consideration of the interaction with other additives, have not been clarified in detail. We have reported on the effects of PEG and Cl^-, and SPS, and found that the bottom-up growth is considered to be relevant to the SPS concentration-dependent acceleration of copper deposition. In this study, we focused on the effect of JGB in the bath containing four additives (Cl-PEG-SPS-JGB bath). The mechanism of superfilling in this system was discussed from practical trench-filling studies and basic polarization measurements.[2]

The baths containing $CuSO_4$ and H_2SO_4 with various combinations of additives were used. Filling studies were performed with a paddle plating system. Cross sections of copper-filled trenches were observed by a scanning electron microscopy (SEM). Polarization measurements were carried out using a copper rotating disk electrode (RDE) at various rotation speeds.

From cross-sectional SEM images (Figs. 1a and b), the addition of JGB to Cl-PEG-SPS bath decreases the thickness of deposits above copper-filled trenches while the bumps above each trench becames obvious. The bumps became smaller with increase in JGB concentration. However, further addition of JGB resulted in the seam-formation in the trenches. The inhibition of copper deposition above the trenches and its JGB-concentration dependence should be related to the shift of polarization curves toward negative direction with the addition of JGB (Fig. 2).

Agitation of the bath was effective for the leveling of the bumps, while little effect was observed for the bottom-up growth of copper in trenches (Fig. 1c). Because the influence of agitation on the filling feature of copper was not observed for the other JGB-free baths, the effect of the agitation should be attributed to the enhanced transfer of JGB to the copper surface. Since agitation is assumed to provide little effect on the fluid flow condition inside trenches, the enhancement of JGB-transfer by agitation is supposed to be insignificant at the outside of trenches compared with the inside of them. Thus, agitation of the bath would bring about leveling of the surface above copper-filled trenches without disturbing the bottom-up growth. The results of polarization measurements for Cl-PEG-SPS-JGB bath performed with various rotation speeds of RDE (Fig. 3) also supported this hypothesis. The polarization curves with the rotation of RDE shifted toward more negative direction, compared with a polarization curve obtained in a static bath. This negative shift was considered to result from the enhancement of the inhibition of copper deposition with increase in mass-transfer of JGB molecules to the electrode.

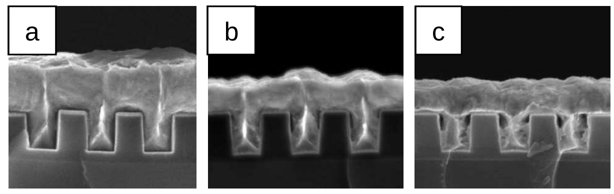

Figure 1. SEM images of copper-filled trenches from Cl-PEG-SPS-JGB baths with (a) 0- and (b and c) 2-ppm JGB. Agitation speeds were (a and b) 0 and (c) 100 rpm.

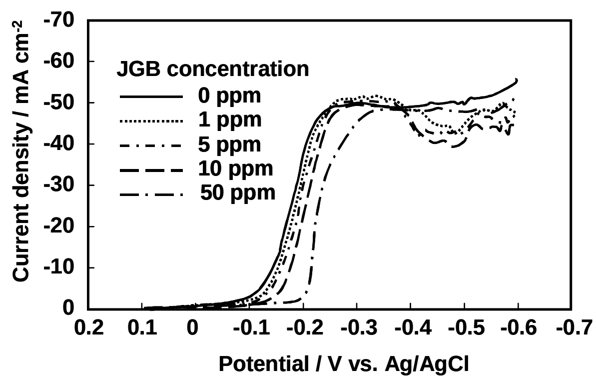

Figure 2. Cathodic polarization curves for copper electrodeposition from Cl-PEG-SPS-JGB baths with various JGB concentrations.

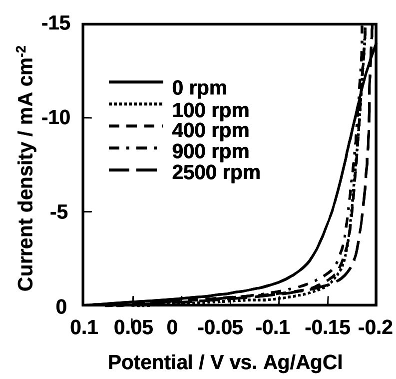

Figure 3. Dependence of polarization characteristics for Cl-PEG-SPS-JGB bath on rotation speeds of RDE.

Acknowledgements

This work was carried out under the 21st Century COE program “Center for Practical Nano-Chemistry”. This work was supported by the Grant-in-Aids for COE Research “Molecular Nano-Engineering” from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

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