

Short Communication

Effect of Additive Triblock Copolymer EPE-8000 on Bottom-up Filling in Copper Electroplating

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The effect of triblock copolymer EPE upon the microvia filling by Cu electrodeposition was investigated by cross-sectional images using optical microscopy. The bottom-up filling of the electroplating bath was achieved with an addition of EPE. The electrochemical study indicated that the polarisation on the cathode was increased with an addition of EPE. Furthermore, X-ray diffraction analyses showed the crystallography and the peak intensity ratio $I(111)/I(200)$ of plated Cu film were decreased with addition of EPE. The surface roughness of deposited Cu film was decreased, and a smooth surface was obtained as the EPE added. The results present EPE-8000 as an inhibitor which is beneficial for microvias filling for high density interconnections printed circuit board.

Keywords: Triblock copolymer; bottom-up filling; electroplating

1. INTRODUCTION

With the progress of development of electronic devices, the number of electronic devices on the chip and circuit densities has increased significantly; Cu electrodeposition in the damascene process for the metallisation of semiconductor interconnects has been used widely for fabricating printed circuit boards (PCBs).[1–3] This is a fabrication process for integrated circuits, including formation of the diffusion barrier, formation of copper seed layer, plating copper and CMP process. However, because the microvias for PCBs are approximately 103 times larger than those for ultra large scale integration interconnects, it is difficult for the Cu electrodeposition solution used in the damascene process to obtain a void-free filling for PCBs.[4] A complete filling of microvias by Cu electroplating is a challenge in the fabrication of Cu interconnects of PCB with high density interconnections. In order to guarantee good quality interconnects of PCB, void-free filling, or the so called bottom-up filling, in which the Cu deposition rate at the bottom of the microvia is faster than

that at the top, must be achieved.[5] Several additives, such as chloride ions (Cl^-), polyethylene glycol (PEG) as a suppressor, and bis(3-sulphopropyl)disulphide (SPS) as an accelerator, are incorporated in the Cu electroplating bath and assist in the direct current plating of Cu to accomplish bottom up filling for PCBs.[6,7] Although there are many reports in the literature focused on understanding superfilling for fabricating Cu interconnects in ultra large scale integration,[8] the research in bottom-up filling for PCBs is slim. Only Honma et al.[2] and Dow et al.[5–7] have reported via-filling using electroplating for PCBs.

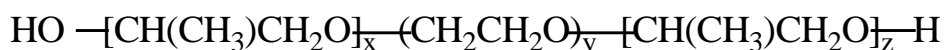
For the electroplating Cu solution in the damascene process, the additives PEG and Cl^- adsorb preferentially on the outside of microvias and inhibit the Cu electrodeposition, and SPS adsorbs at the bottom of microvias and accelerates the Cu electrodeposition in the superfilling of Cu electrodeposition.[9,10] The bottom_up filling of copper electroplating was achieved with an addition of triblock copolymer as an inhibitor to fill 100-nm microvias [11], but the bottom_up filling of copper electroplating was not obtained with an addition of triblock copolymer with propylene oxide terminal blocks termed EPE as an inhibitor to fill 50- μm microvias.

Triblock copolymers EPE had strong inhibition for Cu electrodeposition and were used as suppressor in the superfilling of Cu electrodeposition [12, 13], but the copper filling of EPE as suppressor of a three-additive system has not been reported.

In this article, we address the copper filling of 50 μm microvias using triblock copolymer EPE-8000 as suppressor. And the effect of EPE-8000 on the crystallography was studied.

2. EXPERIMENTAL

EPE-8000, known by the trade name Pluronic[®] PE6800 (BASF AG), was nonionic surfactant and made up from ethylene oxide (EO) 80%, which is relatively hydrophilic, and propylene oxide (PO) 20%, which is relatively hydrophobic [14]. With the molecular weight of a PO repeat unit being 58 g mol^{-1} and an EO repeat unit being 44 g mol^{-1} , an EPE-8000 molecule is calculated to contain an average of 56.8 sticking points per molecule (about 145.5 EO repeat unit and 27.6 PO repeat unit). The molecular structure of EPE-8000 is shown as follows.



Microvias with diameter of 50 μm and depth of 50 μm were used in the experiments. All solutions were prepared using reagent grade chemicals and deionised water. Before electroless Cu plating, the surface of the epoxy resin laminate was pretreated with reagent grade chemicals and deionised water. Before electroless Cu plating, the surface of the epoxy resin laminate was pretreated.

To investigate the effect of EPE-8000 on microvia filling characteristics, the cross-sectional images of the microvias were observed by an optical microscope (OM). As shown in Fig. 1, the filling capability of a microvia is expressed as a filling performance. Height from the bottom of a microvia to the deposited Cu surface and Cu film thickness at the centre of the microvias are expressed as H1 and

H2 respectively; the filling performance calculated by a proportion of H₂ to H1. Linear sweep voltammetry was performed to analyze the effect of EPE-8000 on cathodic polarisation of the electrolyte for Cu deposition. In the electrochemical analyses, a ϕ 3.0 mm pure Cu electrode was used as the working electrode, and a 1×1 cm² platinum sheet and a commercial electrode of Ag/AgCl saturated with KCl were used as the counter and reference electrodes, respectively.

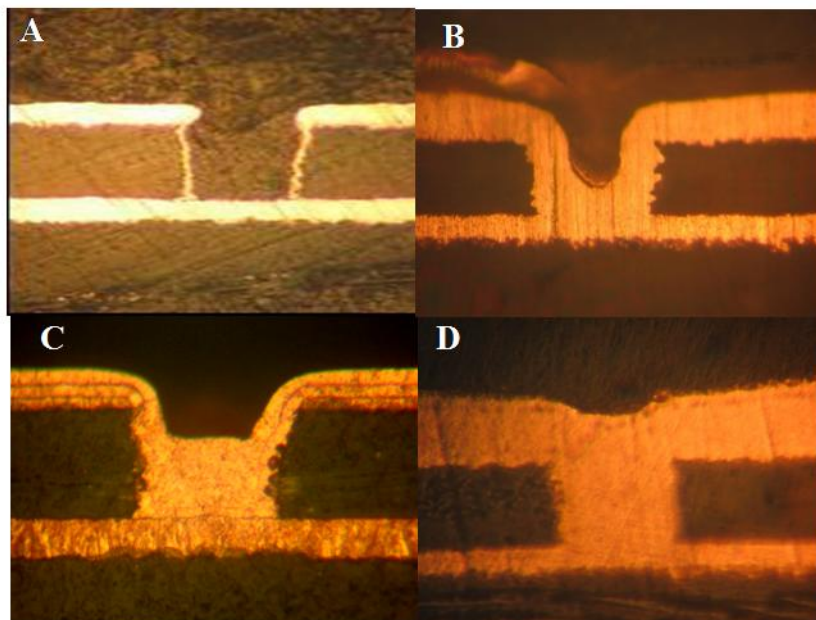


Figure 1. Cross-sectional OM images of holes with different plating times. Plating times: (A) 0 min, (B) 30 min, (C) 60 min, (D)80 min

Linear sweep voltammetry experiments were carried out at 25 °C and at a scan rate of 10 mV s⁻¹ in the range from 0 to -0.6 V. The electrolyte was composed of 0.8 mol L⁻¹ CuSO₄·5H₂O, 0.53 mol L⁻¹ H₂SO₄, 50 ppm Cl₂ and 350 ppm EPE-8000.

The crystalline structures of plated Cu films were measured by an X-ray diffractometer (Dmax3C Rigaku) using 2 θ scan with a Cu Ka source working at 40 kV and 40 mA.

3. RESULTS AND DISCUSSION

In order to achieve a complete bottom-up filling of electroplating copper, the effects of the inhibitor on the bottom-up filling of microvias should be first investigated.

Figure 1 shows cross-sectional OM images of 50 μ m microvias filled by electrodeposition of Cu in the bath. Figure 1A shows the cross-sectional OM image of the hole before electrodeposition. After plating for 30 min (Fig. 1B) a somewhat conformal filling was obtained, and 60 min (Fig. 1C), a significant bottom-up filling of electroplated Cu in the microvia was observed. Further to that, void-free filling of Cu was completed after electroplating for 80 min (Fig. 1D), and a bottom-up filling was obtained.

It was noted that thickness of Cu on the top surface changes significantly over plating time. The deposition rate of Cu on the top surface was very small before microvias had been filled by plated Cu. After the microvias were almost filled with Cu, the thickness of Cu on the top surface started to increase noticeably. This was attributed to EPE-Cl⁻ suppressing mainly Cu deposition on the surface of the substrate, and the acceleration of SPS-Cl⁻ acting at the bottom of microvias before they had been filled in plating of Cu. When the microvias were almost filled with Cu, the combined effects of SPS-Cl⁻ and EPE-Cl⁻ cause the deposition rate of plating of Cu on the surface of the substrate to increase.

This result may be explained by the following: According to the filling mechanism [15], the inhibition of copper deposition by the suppressor (EPE-Cl⁻) at the board surface was inadequate. Suppressor (EPE-Cl⁻) has a large molecular weight and low diffusion rate in electroplating solution, and it is adsorbed onto a copper surface of substrate in the form of monolayer. Though the molecular weights of SPS-Cl⁻ were near 400, the diffusion coefficients of SPS-Cl⁻ should be larger than that of EPE-Cl⁻ because of large molecular weight of EPE. The acceleration of copper deposition by the accelerator (SPS-Cl⁻) at the microvia bottom was strong under the plating condition, and so bottom-up filling of copper was accomplished.

In order to explore the effect of EPE for copper deposition, linear sweep voltammetry measurement was used to investigate the effects of EPE on the polarization curves of the electroplating solution (Fig.2).

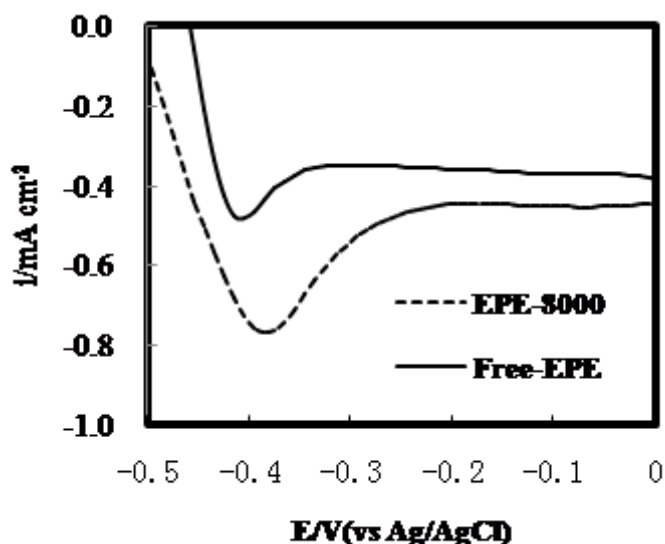


Figure 2. Effect of EPE-8000 on the cathodic polarization behavior of electrolyte for copper plating

Effects of EPE on the cathodic polarisation of the electroplating bath were investigated by linear sweep voltammetry, and the results are shown in Fig. 2. From Fig. 2, it was found that copper reduction current changed with addition of EPE. The reduction peak current and peak potential were about $-0.476 \text{ Am cm}^{-2}$ and -0.415 V without addition of EPE, it shifted to $-0.766 \text{ Am cm}^{-2}$ and -0.385 V with 350 mg L^{-1} EPE addition. It may be attributed to the strength of EPE adsorption on the Cu surface with addition of EPE.

The crystallography of superfilling plated Cu films, which deposited from the plating solution in the absence and presence of EPE, were characterized by XRD (Figure 3). When EPE was added in bath, the peak intensity ratio $I(111)/I(200)$ was 2.6, and the full-width at half-maximum (FWHM) of (111) for 2.2 μm thick Cu film was 0.24° . For plated Cu film without additives, the peak intensity ratio $I(111)/I(200)$ was 4.4 and FWHM of (111) for 2.2 μm thick Cu film was 0.21° , which indicated that the crystallinity and peak intensity ratio $I(111)/I(200)$ were decreased with addition of EPE.

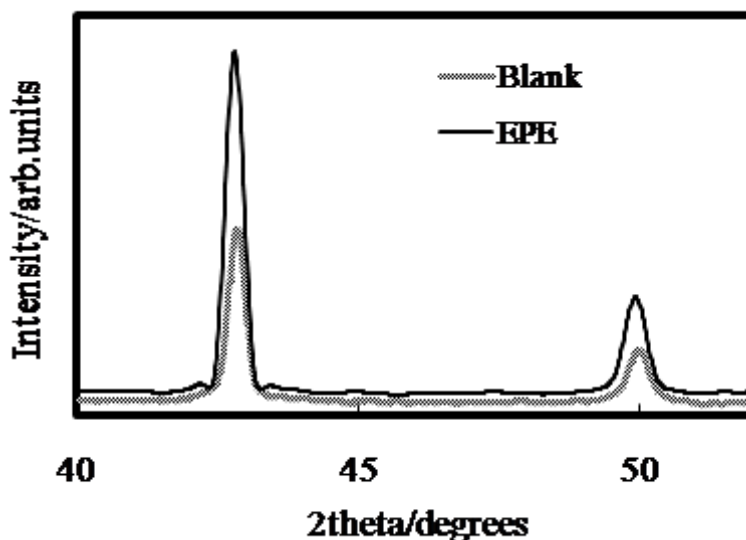


Figure 3. XRD patterns of plated Cu films.

According to Scherrer formula [14], the results indicated the crystallinity of plated Cu film was reduced by addition of EPE, but peak intensity ratio $I(111)/I(200)$ was increased upon addition of EPE. It is well known that the copper film with a strong (111) texture can enhance electromigration resistivity performance because of the reduced degree of anisotropy in grain boundary transport. Consequently, the performance of the plated Cu films was improved by an addition of EPE.

4. CONCLUSIONS

The effect of EPE as an additive on bottom-up filling characteristics in copper deposition was investigated. Bottom-up fillings with microvias of 50 μm and aspect ratio of one were obtained in the electroplating Cu bath with addition of EPE-8000. Linear sweep voltammetry measurement indicated that EPE-8000 inhibited on Cu deposition, which is in agreement with the results of cross-sectional OM observation. The crystallinity and the peak intensity ratio $I(111)/I(200)$ of plated Cu films were decreased with an addition of EPE-8000; the surface of electroplated Cu films become more smooth with an addition of EPE-8000. From the results obtained in this study, it is concluded that EPE-8000 was highly effective for void-free filling of trenches.

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References

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans and H. Deligianni, *IBM J. Res. Dev.*, 42(1998) 567.
2. T. Kobayashi, J. Kawasaki, K. Mihara and H. Honma, *Electrochim. Acta.*, 47(2001)85.
3. W. P. Dow, H. S. Huang and Z. Lin, *Electrochem. Solid State Lett.*, 6(2003)C134.
4. S. Miura, H. Honma, *Surf. Coat. Technol.*, 169(2003)91.
5. W. P. Dow, M. Y. Yen, W. B. Li, and S. W. Ho, *J. Electrochem. Soc.*, 152(2005)C769.
6. W. P. Dow, H. S. Huang, M. Y. Yen and H. C. Huang, *J. Electrochem. Soc.*, 152(2005)C425.
7. W. P. Dow, M. Y. Yen, C. W. Liu and C. C. Huang, *Electrochim. Acta*, 53(2008)3610.
8. S. K. Kim, J. J. Kim, *Electrochem. Solid State Lett.*, 7(2004)C98.
9. K. Kondo, T. Matsumoto and K. Watanabe, *J. Electrochem. Soc.*, 151(2004)C250.
10. A. Pohjoranta and R. Tenno, *J. Electrochem. Soc.*, 154(2007)D502.
11. J. W. Gallaway, M. J. Willey, A. C. West, *J. Electrochem. Soc.*, 156 (2009)D146.
12. J. W. Gallaway, M. J. Willey, A. C. West, *J. Electrochem. Soc.*, 156(2009) D287.
13. J. W. Gallaway, A. C. West, *J. Electrochem. Soc.*, 155(2008) D632.
14. C. H. Lee, A. R. Kim, H-C Koo, J. J. Kim, *J. Electrochem. Soc.*, 156(2009) D207.
15. K. Shimada, H. Kato, T. Saito, S. Matsuyama, and S. Kinugasa, *J. Chem. Phys.*, 122(2005) 244914.