Effect of 3-S-isothiuronium propyl sulfonate on bottom-up filling in copper electroplating

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Abstract

The effect of 3-S-isothiuronium propyl sulfonate (UPS) upon the microholes 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 UPS. The electrochemical study indicated that the polarisation on the cathode was decreased with an addition of UPS. 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 UPS. The results present UPS as an accelerator which is beneficial for microholes filling for high density interconnections printed circuit board.

Keywords: Damascene copper plating, accelerator, Microhole filling

1 Introduction

Depolarizers (accelerators, anti-suppressors) belong to one important class of copper plating additives that are used in the integrated circuit (IC) industry for the on-chip metallization of holes and trenches [1]. It is the non-uniform distribution of such accelerators and suppressor additives across those trenches and holes that allow their superfilling with copper. Origin of these non-uniformities in the additive surface coverage is the conjunction of purely geometric shape evolution effects upon fill with the distinct transportation and adsorption kinetics of the depolarizer and suppressor additives involved [2–5].

Most common suppressor used for the Damascene process is polyethyleneglycol (PEG) that are known to form barriers for cupric ions on the copper surface when combined with chloride [6–12]. Sulfur-containing, organic additives typically serve as depolarizers. Bis (3-sulfopropyl) disulfide (SPS) is the most widely used depolarizer for Damascene applications [3,12]. SPS shows such a mild depolarizing effect on the copper deposition, but only when chloride is present as a co-additive [8, 13]. Such intrinsic acceleration therefore needs to be considered as a synergistic effect of the SPS and the chloride.

It was reported that other good accelerator was 3-N, N-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS) [14], 3,3-thiobis-1-propanesulfonate (TBPS) [15], 3-mercapto-1-propanesulfonic acid (MPS) [16-18], as potential substitutes of the SPS.

UPS had been used as brightener for Cu electrodeposition [19] and as stabilizer for electroless nickel deposition [20], but the copper filling of UPS as accelerator of a three-additive system has not been reported.

In this article, we address the copper filling of 50 μm microholes using UPS as accelerator. And the effect of UPS on the crystallography was studied.

2 Experimental

PCB fragments with many microholes formed by CO2 laser ablation were used as plating samples. The dimensions of the PCB fragment were 45 mm × 60 mm. The diameters of the microholes were 50 μm. The depth of the microholes was 50 μm. Before metallization, the microholes were conducted through a so-called desmear process in order to remove the smear that was formed by laser ablation at the microhole bottom. The desmear process could thoroughly clean the via bottom to make sure of its conductivity. Following the treatment of desmear process, electroless copper plating was used for sidewall metallization of the microhole. Following that, an electroplated copper layer with a thickness of 2–3 μm was deposited on the sidewall in order to increase the thickness of electroless copper layer for prevention of electroless copper oxidation.

The PCB fragment was plated at a current density of 1.5A dm−2 for 120 min. Two phosphorus-containing copper plates were used as anodes and placed directly in the plating bath with a working volume of 700 mL. The plating solution was constantly agitated by continuously flowing air bubbles at a flow rate of 2.5Lh−1 during the electroplating to ensure good convection.

The electroplating solution used for microhole filling experiments was composed of 220 g L^{-1} $CuSO_4 \cdot 5H_2O$, 55 g L^{-1} H_2SO_4, 12 ppm 3-S-isothiuronium propyl sulfonate (UPS), 4 ppm Janus Green B (JGB) aswell as Cl^- (added as NaCl), 300ppm PEG-8000. Temperature of the plating solution was controlled at 25℃. The filling performance of the plating bath was evaluated by cross-sectional views of the microholes using optical microscopy (DFC290, Leica) at a magnification of 200×.

To investigate the effect of UPS concentration on microhole filling characteristics, the cross-sectional images of the holes were observed by an optical microscope (OM). As shown in Fig. 1, the filling capability of a microhole is expressed as a filling performance. Height from the bottom of a via-hole to the deposited Cu surface and Cu film

thickness at the centre of the microholes are expressed as H_1 and H_2 respectively; the filling performance calculated by a proportion of H_2 to H_1. Linear sweep voltammetry was performed to analyse the effect of UPS concentration on cathodic polarisation of the electrolyte for Cu deposition. In the electrochemical analyses, a φ3.0 mm pure Cu electrode was used as the working electrode, and a 10×10 mm^2 platinum sheet and a commercial electrode of Ag/AgCl saturated with KCl were used as the counter and reference electrodes, respectively. Linear sweep voltammetry experiments were carried out at 25℃ and at a scan rate of 10 mV s−1 in the range from 0 to −0.6 V.

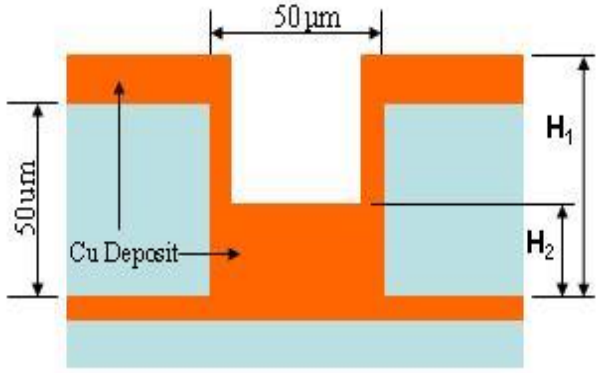

FIGURE 1 Filling Power of microhole

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

3 Results and discussion

To investigate the effect of UPS concentration on microholes filling characteristics, the cross-sectional images of the microholes were observed by an optical microscope (OM). Figure 2A shows the cross-sectional OM image of the hole before electrodeposition. After plating for 30 min (Fig. 2B) a somewhat conformal filling was obtained, and 60 min (Fig. 2C), a significant bottom-up filling of electroplated Cu in the microhole was observed. Further to that, void-free filling of Cu was completed after electroplating for 80 min (Fig. 2D), 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 microhole had been filled by plated Cu. After the microhole were almost filled with Cu, the thickness of Cu on the top surface started to increase noticeably. According to N. T. M. Hai [15], this was attributed to PEG-Cl^- suppressing mainly Cu deposition on the surface of the substrate, and the acceleration of UPS-Cl^- acting at the bottom of microhole before they had been filled in plating of Cu. When the microhole were almost filled with Cu, the combined effects of UPS-Cl^- and PEG-Cl− cause the deposition rate of plating of Cu on the surface of the substrate to increase.

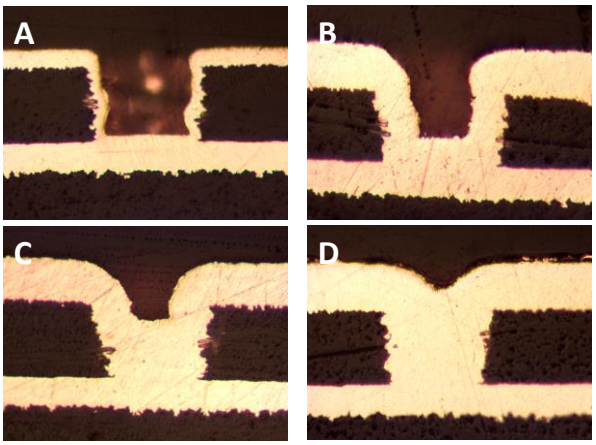

FIGURE 2 Cross-sectional OM images of holes with different plating times. Plating times: (A) 0 min, (B) 30 min, (C) 60 min, (D)80 min

Effects of UPS concentration on the cathodic polarisation of the electroplating bath were investigated by linear sweep voltammetry, and the results are shown in Figure 3.

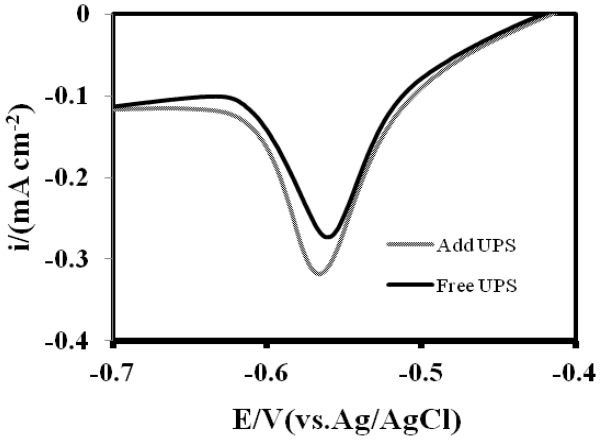

FIGURE 3 Effect of EPE-8000 on the cathodic polarization behavior of electrolyte for copper plating

From Fig. 3, it was found that copper reduction current changed with addition of UPS. The reduction peak current was about -0.269 Am cm^{-2} without addition of UPS, it shifted to -0.319 Am cm^{-2} with 12 mg L^{-1} UPS addition, but copper reduction potential did not change obviously with addition of the UPS. As mentioned above, the change of the reduction peak current of copper with an addition of UPS was significant agreement with the tendency that of copper deposition with the tendency that copper deposition with an addition of UPS, which in-depth indicated that copper reduction reaction was accelerated by addition of UPS.

The crystallography of superfilling plated Cu films, which deposited from the plating solution in the absence and presence of UPS, were characterized by XRD. When UPS was added in bath, the peak intensity ratio I(111)/I(200) was 4.6, and the full-width at half-maximum (FWHM) of (111) for 3.0 μm thick Cu film was 0.21°. For plated Cu film without additives, the peak intensity ratio I(111)/I(200) was 2.4 and FWHM of (111) for 3.2 μm thick Cu film was 0.27°, which indicated that the crystallinity and peak intensity ratio I(111)/I(200) were

increased with addition of UPS. According to Scherrer formula [21], the results indicated the crystallinity of plated Cu film was reduced by addition of UPS, but peak intensity ratio I(111)/I(200) was decreased upon addition of UPS. 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 UPS.

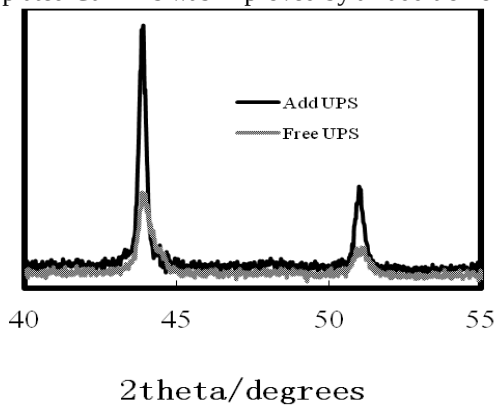

FIGURE 4 XRD patterns of plated Cu films

4 Conclusions

The effect of UPS as an additive on bottom-up filling characteristics in copper deposition was investigated. Bottom-up fillings with microholes of 50 μm and aspect ratio of one were obtained in the electroplating Cu bath with addition of UPS. Linear sweep voltammetry measurement indicated that UPS accelerated 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 increased with an addition of UPS; the surface of electroplated Cu films become more smooth with an addition of UPS. From the results obtained in this study, it is concluded that UPS was highly effective for void-free filling of trenches.

Acknowledgments

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