

Bottom-Up Filling in Electroless Plating with an Addition of Janus Green B and Triblock copolymers PEP-3100

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The bottom-up filling of electroless copper usually depends on inhibiting the surface deposition of electroless copper or accelerating to achieve a relative high deposition rate of electroless copper in the bottom of trenches. In this paper, a bottom-up filling of electroless copper, in which the deposition rates of electroless copper were inhibited at the surface of the substrate and accelerated in the bottom of the trench, was designed and achieved in the bath with an addition of Janus Green B (JGB) and Triblock copolymers PEP-3100. The cross-section SEM observation indicated that all trenches with different widths ranging from 130 to 520 nm were filled completely by electroless copper and no void was found. This was attributed to synergistic effect of three factors, addition JGB only in the bath accelerated Cu deposition markedly; addition bath JGB and PEP-3100 in the bath decreased Cu deposition sharply; the large molecular weight and lower diffusion coefficient of PEP-3100 resulted in concentration gradient of PEP-3100 in the trenches. The effects of PEP-3100 and JGB on both cathodic and anodic reaction were demonstrated by linear sweep voltammetry (LSV) method.

Keywords: bottom-up fill; electroless deposition; additives; synergistic effect; PEP-3100

1. INTRODUCTION

Cu electroless deposition had been mainly used for metal interconnects of printed circuit boards (PCBs) owing to its advantages. The bottom-up fill of copper by electroless deposition has been demonstrated with a plating bath containing a deposition inhibitor or accelerator. Shingubara et al.[1-3] first achieved void-free filling of high aspect ratio via-holes with the addition of bis-3-sulfopropyl-disulfide (SPS) as inhibitor and polyethylene glycol (PEG) as surface activator in plating bath containing glyoxylic acid as inducing agent, and then investigated on the bottom-up filling behavior of the plating bath containing the mercapto alkyl carboxylic acids[4-5]. M. Hasegawa et al. achieved void-free electroless copper deposition in submicrometer trenches in the presence of the single PEG as inhibitor and glyoxylic acid as inducing agent[6], and also achieved void-free filling with an addition

of 8-hydroxy-7-iodo-5-quinoline sulfonic acid (HIQSA) as accelerator and PEG as inhibitor in plating bath containing formaldehyde as inducing agent [7-8]. Triblock copolymers had strong inhibition for Cu electrodeposition and were used as suppressors in the superfilling of Cu electrodeposition [9-10]. Yang et al. achieved void-free filling with an addition of PEG-PPG triblock copolymers as inhibitor and formaldehyde as inducing agent [11]. Wang et al. achieved void-free filling with an addition of PEP-3100 triblock copolymers as inhibitor and glyoxalic acid as inducing agent [12]. Kim et al. also reported that void-free filling was achieved with SPS as accelerator [13-14], its derivatives, 3-N,N-dimethylaminodithiocarbamoyl-1-propanesulfonic acid (DPS) [15] and 2-Mercapto-5-benzimidazolesulfonic Acid (MBIS) [16], which all accelerated the deposition rate at very low concentrations.

The achievement of the above-mentioned bottom-up filling of electroless copper depended on inhibiting the deposition rate of Cu at the surface of substrate or accelerating the deposition rate of Cu at the bottom of substrate to obtain a relative high deposition rate of electroless Cu in the bottom of holes or trenches, but the ratio of deposition rate in the bottom and at the opening of trenches was relatively small.

In order to fill high aspect ratio via-holes completely, a real bottom-up filling of electroless copper, in which the deposition rates of electroless copper were inhibited at the surface of the substrate and accelerated in the bottom of the trench, was designed and investigated in plating bath with an addition of JGB and PEP-3100. The synergy effects of JGB and PEP-3100 on the bottom-up filling of trenches by electroless copper deposition were researched in detail by deposition rate measurements and by cross-sectional SEM observations.

2. EXPERIMENTAL

For the trench-filling experiments, SiO₂/Si substrates with trench arrays were employed. The trench patterns (width 110-380 nm, depth 470-520 nm) were used to investigate bottom-up filling of electroless copper. A layer of tantalum metal (10 nm) and a copper seed layer (40 nm) were deposited onto the substrates by physical vapor deposition (PVD). The substrates were pretreated with 1 M H₂SO₄ for 5 min to remove the native Cu oxide (including about 1 min ultrasonication), rinsed in ultrapure water, and immersed into a plating bath. After the deposition, the filling feature in cross-sectioned trenches was examined by a field emission scanning electron microscope (FE-SEM, JSM-6700 F).

The composition of the electroless copper plating solution was: CuSO₄·5H₂O (6.0 g L⁻¹), C₁₀H₁₆N₈O₈ (Na₂EDTA 30.0 g L⁻¹), glyoxylic acid (10.0 g L⁻¹) as a reducing agent, PEP-3100 (Average molecular weights about 3100MW) as inhibitor, Janus Green B (JGB) as accelerator. The pH of the plating bath was adjusted to approximately 12.5 using sodium hydroxide (NaOH) and the bath temperature was maintained at 70 °C.

Copper deposition rates were determined by the change in weight of ABS boards after 60 min plating assuming uniform plating and bulk density, compared to its weight before pretreatment. The crystalline structures of electroless plated Cu films were measured by an X-ray diffractometer (XRD,

Dmax3C Rigaku) using θ - 2θ scan with a Cu $K\alpha$ source working at 40 kV and 40 mA. The interfacial structure and morphology of samples were characterized by field-emission scanning image microscopy (FE-SIM, JSM-6700F).

For Linear sweep voltammetry, a ϕ 3.0 mm pure copper electrode was used as the working electrode, and 4.0 cm² platinum sheet and a commercial electrode of Hg/Hg₂Cl₂ were used as the counter and reference electrodes, respectively. Linear sweep voltammetry (LSV) experiments were carried out at 25 °C and at a scan rate of 15 mV s⁻¹. The anodic polarization curves were measured from the glyoxylic-acid -reduction electroless copper bath in the absence of copper ion, and the cathodic polarization curves were measured from the same composition bath without glyoxylic acid.

3. RESULTS AND DISCUSSION

In order to achieve a complete bottom-up filling of electroless copper, the synergy effects of the accelerator including JGB and SPS, and triblock copolymers PEP-3100 on the bottom-up filling of trenches should be first investigated. And the synergy effects were only found in the plating bath with an addition of JGB and PEP-3100. Then the effects of JGB, PEP-3100, PEP-3100 and JGB on the deposition rate of electroless copper were researched when the deposition time was 60 min. The deposition rate of electroless copper plating increased rapidly with an initial addition of JGB, thereafter, the deposition rate of electroless copper plating increased gradually with an increase in JGB concentration from 0.1 to 0.3 mg L⁻¹ and decreased gradually with an increase in JGB concentration from 0.3 to 0.5 mg L⁻¹, the deposition rate of electroless copper was lower than that of the JGB-free (Fig. 1), which indicated that an addition of JGB at low concentration accelerated and at high concentration inhibited electroless copper deposition.

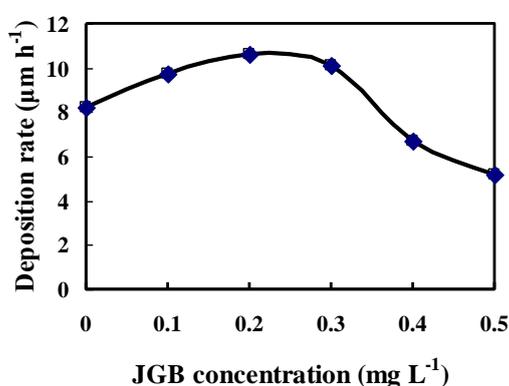


Figure 1. The effect of JGB concentration on the deposition rate.

On the other hand, when PEP-3100 concentration in electroless copper bath changed from 0 to 1.0 mg L⁻¹, the deposition rate of electroless copper decreased from 8.2 to 2.1 μm h⁻¹ and declined about 70% (Fig. 2). However, when JGB concentration in the plating bath was 0.3 mg L⁻¹, the

inhibition of PEP-3100 for electroless copper deposition became more strongly. The deposition rate of electroless copper decreased from 9.6 to 1.3 $\mu\text{m h}^{-1}$ with PEP-3100 concentration from 0 to 1 mg L^{-1} , about 90% decline, which means that when PEP-3100 concentration in the bottom of trenches was near to zero, the deposition rate of electroless copper in the bottom of the trenches was 8 times higher than at the surface or opening of trenches, and perfect bottom-up filling of electroless copper would be able to be obtained.

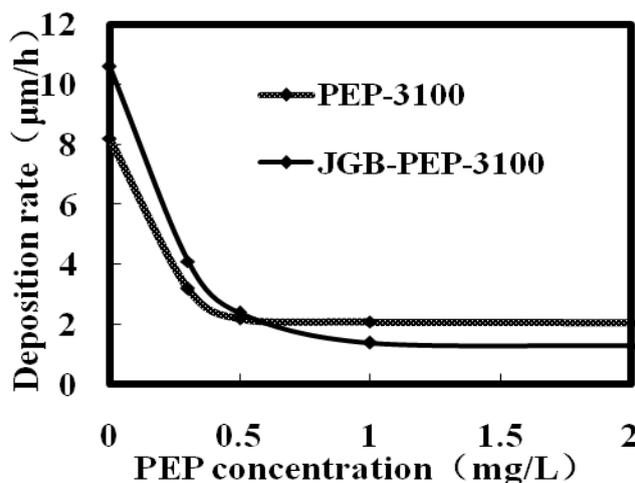


Figure 2. The effect of PEP-3100 concentration and PEP-3100 and JGB concentration on the deposition rate.

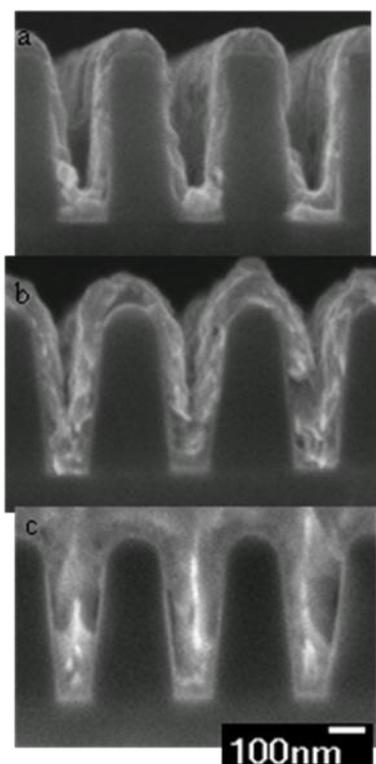


Figure 3. Cross-sectional SEM images of trenches with plating time, trench width: 140 nm, trench depth: 470 nm. Plating times: (a) 1 min, (b) 3 min, (c) 7 min

According to the above-mentioned experiment results, the trenches with a width of 140 nm and depth of 470 nm were used to examine bottom-up filling of electroless copper with plating time, and the bottom-up filling characteristics of plating bath containing 0.3 mg L^{-1} JGB and 1 mg L^{-1} PEP-3100 was studied by cross-sectional SEM observation and the results were shown in Fig. 3.

At a plating time of 1 min, Cu thickness at the surface (T_s) and at the bottom of trench (T_b) were approximately 57 and 74 nm, respectively; when the plating time was 3 min, T_s and T_b became 87 and 216 nm, respectively (see Fig. 3a and 3b). These results indicated that the Cu deposition rate at the bottom of the trench was higher than on the surface at the initial period. The trenches were almost filled with Cu at a plating time of 7 min (Fig. 3c), which suggests that bottom-up filling with electroless plated Cu could be obtained by addition of JGB and PEP-3100 into the electroless Cu plating solution.

This result may be explained by the following: Hideaki Yokoyama et al[17] reported that the molecular weight (M) dependence of D_0 for PEG in water can be expressed as $D_0 \propto \exp(-\alpha M)$, So, the diffusion coefficient of PEP-3100 was less than that of PEP-400, Though the molecular weights of $[\text{Cu}(\text{EDTA})]^{2-}$ was 419 and that of JGB was 511, but the diffusion coefficients of $[\text{Cu}(\text{EDTA})]^{2-}$ and JGB should be larger than that of PEP-400 because of their good solubility in aqueous solution. On the other hand, PEP-3100 prefers to adsorb on the surface of substrate than to enter the sub-micrometer trenches [17-18], which caused a concentration gradation of PEP-3100 in the sub-micrometer trenches, namely resulted in lower concentration of PEP-3100 in the bottom than that at the opening and the surface of the trench. At the same time, JGB has a small molecular weight and high diffusion rate, which caused it distributed evenly in the bottom and the surface of the trench. So the deposition rates of electroless copper on the surface and the opening of trenches were inhibited by high PEP-3100 concentration combined with the JGB. While the deposition rates of electroless copper in the bottom of trenches was accelerated by very low PEP-3100 concentration combined with the JGB.

The suppressor adsorbs on the surface of the trench while it was used alone. The degrading adsorption effect was shown in the addition of an accelerator to a suppressor-containing electrolyte. The accelerator makes the adsorbed layer desorb from the surface. Hence, free surface sites are available for copper deposition.

This adsorptive and inhibitive behavior of PEP-JGB is related with the surface coverage on the copper surface. If PEP was not present in the electrolyte, JGB could not exhibit a strong accelerated effect on copper deposition. If PEP was present in the electrolyte, the synergistic inhibition effect of PEP with JGB occurred. These results suggest that the synergistic inhibition effect caused by the composite suppressor, PEP-JGB. When both PEP and JGB are coadsorbed on the copper surface, the composite suppressor becomes more compact to block copper deposition.

To demonstrate further bottom-up filling, the trenches with the width of 130~520 nm and the depth of 450~770 nm were used to examine bottom-up filling of electroless copper. The various trench-filling characteristics were investigated in the plating bath containing 1.0 mg L^{-1} PEP-3100 and 0.3 mg L^{-1} JGB, and the cross-sectional SEM images of trenches were shown in Fig. 4. All trenches with different width and depth were all filled by electroless copper, and no void was found. This result indicated that the bottom-up filling capability of the plating bath with an addition of 1.0 mg L^{-1} PEP-3100 and 0.3 mg L^{-1} JGB was much strong.

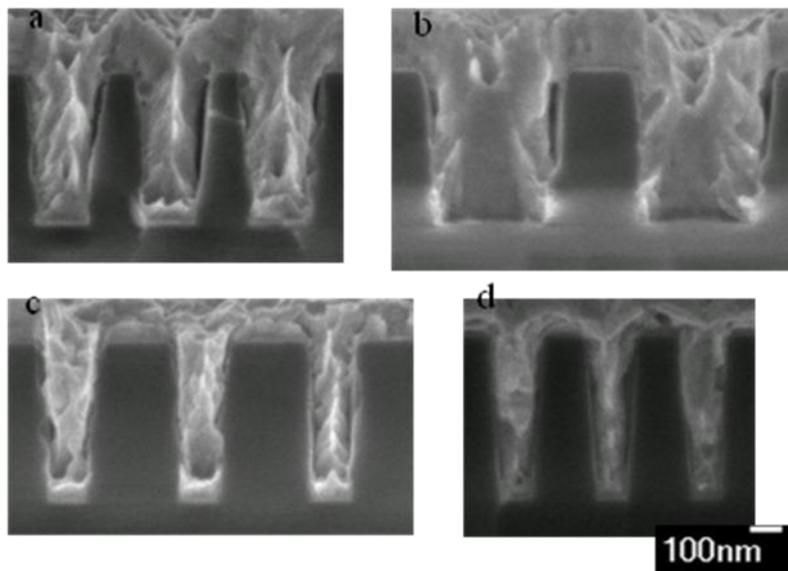
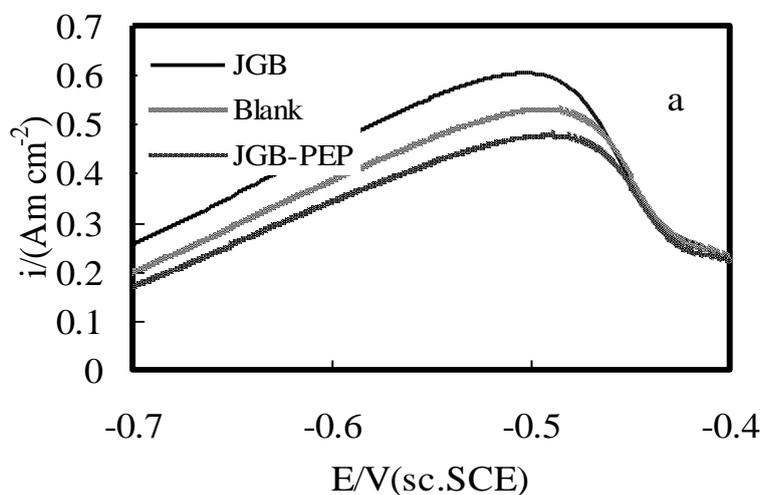


Figure 4. Cross-sectional SEM micrographs of electroless Cu profiles for various trenches, trench width: 110~380 nm, trench depth: 470~520 nm. Trench kinds: (a) trench width 190 nm, trench depth 470 nm, (b) trench width 380 nm,

In order to explore the effect of PEP-3100 and JGB for copper deposition, linear sweep voltammetry measurement was used to investigate the effects of PEP-3100 and JGB on the polarization curves of electroless copper solution (see Fig.5). For the anodic reaction (See Fig. 5a), it was found that peak potential almost changed with an addition of PEP-3100 and JGB, but glyoxylic acid oxidation current changed obviously. The oxidation peak potential of glyoxylic acid was 0.528 Am cm⁻² with additive free, it was increased to 0.601 Am cm⁻² with an addition of 0.3 mg L⁻¹ JGB, it shifted to 0.476 Am cm⁻²) with 1 mg L⁻¹ PEP-3100 and 0.3 mg L⁻¹ JGB addition. For the cathodic reaction (See Fig. 5b), it was found that copper reduction current changed with addition of the additives.



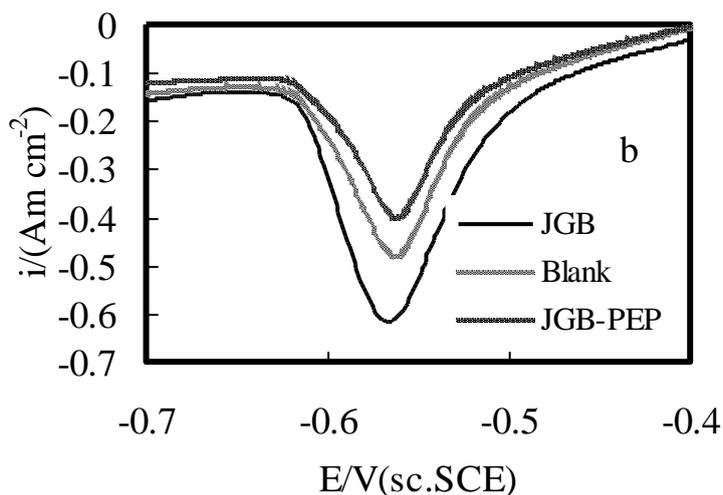


Figure 5. Effect of JGB and PEP-3100 on the polarization behavior of electrolyte for electroless copper plating (a) anodic polarization, (b) cathodic polarization.

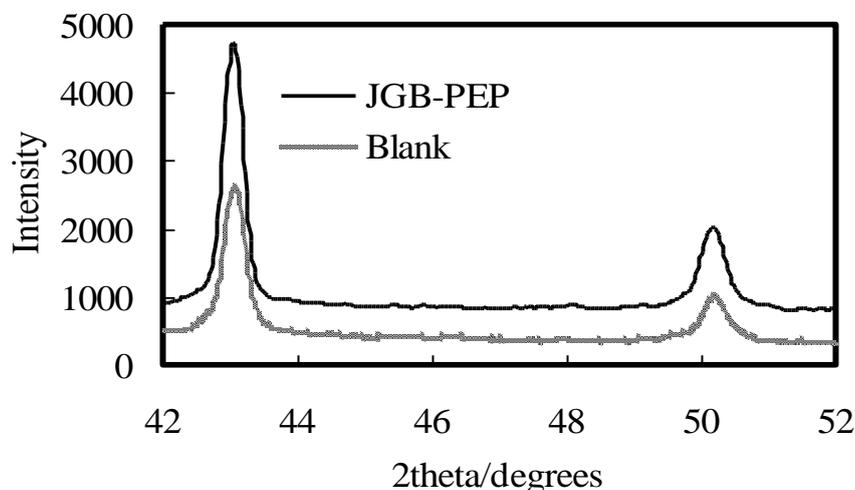


Figure 6. XRD patterns of electroless plated Cu films.

The reduction peak current was about $-0.481 \text{ Am cm}^{-2}$ without addition of the additives, it shifted to $-0.608 \text{ Am cm}^{-2}$ with 0.3 mg L^{-1} JGB addition, and shifted to $-0.395 \text{ Am cm}^{-2}$ with 1 mg L^{-1} PEP-3100 and 0.3 mg L^{-1} JGB addition. According to potential method, both the decrease of reduction and oxidation peak currents and the positive shift of oxidation peak potential result in inhibition for electroless copper deposition, which was agreement with the electroless copper deposition rate and in-depth indicated that copper reduction reaction was inhibited by addition of PEP-3100 and JGB.

The crystallography of superfilling plated Cu films, which deposited from the plating solution in the absence and presence of JGB-PEP-3100, were characterized by XRD (Fig. 6). When the PEP-3100 concentration was 1 mg L^{-1} and JGB concentration was 0.3 mg L^{-1} , the peak intensity ratio $I(111)/I(200)$ was 3.55, and the full-width at half-maximum (FWHM) of (111) for 2.2 mm thick Cu

film was 0.299° . For electroless-plated Cu film without JGB-EPE addition, the peak intensity ratio $I(111)/I(200)$ was 3.15 and FWHM of (111) for 2.2 mm thick Cu film was 0.298° . According to Scherrer formula [16], the results indicated the crystallinity of electroless plated Cu film was reduced by addition of JGB-PEP, peak intensity ratio $I(111)/I(200)$ was increased upon addition of JGB-PEP. 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 electroless plated Cu films was improved by an addition of JGB-PEP.

4. CONCLUSION

The effects of PEP-3100, JGB, both of PEP-3100 and JGB as an additive on the deposition rate and bottom-up filling characteristics in electroless copper solution were investigated. Deposition rate measurements showed that the acceleration of copper deposition by only incorporating JGB at lower concentration, however, the deposition rate abruptly decreased when PEP-3100 and JGB were added to the bath. It was demonstrated that adding JGB and PEP-3100 to the plating bath improved trench-filling properties. The void-free filling achieved in the simultaneous presence of both additives was attributed to the acceleration effect of JGB at the trench bottom and the inhibition effect of PEP-3100 combined with JGB at the trench openings, the latter effect being due to the low diffusion rate of PEP-3100 molecules into the narrow trenches. Electroanalytical measurements showed that the effect of additives were mainly associated with the cathodic reaction. From the results obtained in this study, it is concluded that the combination of the JGB and PEP-3100 was highly effective for void-free filling of trenches.

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