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Copper damascene electrodeposition and additives

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Abstract

Copper via filling is one of the most recent nanoscale electrodeposition technologies used in semiconductor fabrication. Sub micrometer vias on silicon wafers serve as digital signal conductors, when filled with copper. The additives in the electrodeposition bath are critical to obtain vias free of voids and defects. Current–voltage curves show that different additives have either inhibition or acceleration effects. Polyethylene glycol (PEG) and Janus green B (JGB) additives are inhibitors. Scanning electron microscopy images indicate that PEG molecules of about 30 nm in diameter absorb preferentially at the edges of copper macrosteps and inhibit the lateral growth of copper electrodeposits. Rotating disk electrode (RDE) experiments show that higher rotation speeds produce lower deposition current with PEG and JGB additives. Through-mask cathodes to simulate via bottoms were used to simulate the via bottom surfaces so that the enhancement rates could be investigated. With bis(3-sulfopropyl) disulfide (SPS) in addition to chloride ions (Cl^-), PEG and JGB, the current at the simulated via bottom cathode increases. This current also increases with an increase in SPS concentration. This accelerating effect of SPS was found with the typical combination of four additives (Cl^- + PEG + JGB + SPS) used for via filling. The current increases with an increase in aspect ratios of the through-mask cathodes. With a higher aspect ratio of a deeper via, it is proposed that the via bottom accelerating Cu(I)thiolate complex is accumulated at the via bottom. From cross-sectional observations of the deposit thickness, the complex must form during electrolysis, and accumulate at the deeper via bottoms during electrolysis.
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Keywords: Electrodeposition; Copper; Additives; Damascene; Via filling

1. Introduction

Recently, on-chip metallization has shifted from an aluminum to a copper process. In the copper damascene process, the copper is electrodeposited into sub micrometer blind vias and trenches. Successful via filling requires the use of a combination of additives, e.g. polyethylene glycol (PEG), chloride ions (Cl^-), bis(3-sulfopropyl) disulfide (SPS) and Janus green B (JGB). Recently, larger size vias of several tens of micrometers have been widely used for building up printed circuit boards (PCB) because stacked vias can be achieved.

Yokoi et al. [1] investigated the electrochemical behavior of PEG with current–voltage curves. They proposed that copper ions were held by PEG molecules, and that these PEG molecules could be adsorbed on the copper surface in the presence of Cl^- ion. Farandon et al. [2] proposed the formation of cuprous and thiolate (monomer of SPS) complexes during the copper electrodeposition. Kelly and West [3,4] used a quartz crystal microbalance and electrochemical impedance spectroscopy and found that PEG inhibits the copper electrodeposition reaction in the presence of Cl^-. Kelly et al. [5] further measured the current–voltage curves for PEG, Cl^-, SPS, and JGB. They were unable to find an accelerating effect of SPS with typical combinations of the four additives (Cl^- + PEG + JGB + SPS) used for via filling. Andricacos et al. [6] calculated the current distribution of damascene electrodeposition with additives. Their calculation was based on an inhibiting additive model of diffusion control. Kondo et al. [7] recently interpreted the current distribution during via filling in terms of regions in the current–voltage curves. Adsorbed PEG molecules of about 30 nm in diameter were observed by field-emission scanning electron microscopy (FESEM) for the first time by Kondo et

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al. [8,9]. These molecules preferentially absorb at the edges of macrosteps and inhibit the lateral growth of copper electrodeposit.

Deligianni et al. [10] recently suggested that with an inhibition additive model the plating time in the shape evolution sequence could not be predicted accurately. Reid et al. [11] proposed that organic additives with sulfur atoms, such as SPS, locally accelerate the current where they adsorb. They further suggested the accumulation of accelerating species on the electrodeposit surface, but no experimental data were shown. West et al. [12] and Josell et al. [13] recently reported acceleration models, which can predict bump formation. These acceleration models are based on the adsorption of accelerator additive.

The objective of this paper is to report detailed experimental results on copper electrodeposits for damascene electrodeposition with additives. The electrodeposit morphology was observed in detail by FESEM. We further used through-mask cathodes in order to simulate the accelerating additive effect at the via bottom surfaces.

2. Experimental

Table 1 shows the bath composition. The basic bath consisted of $CuSO_4$ and H_2SO_4 of 0.6×10^3 and 1.85×10^3 mol m^{-3}, respectively. The additives were Cl^-, 7500 molar mass PEG and JGB, and their concentrations are shown in Table 1. The baths were used for experiments more than 1 h after the bath preparation.

Initially, the current–voltage curves were measured with a rotating disk electrode (RDE) with a diameter of 12 mm to show the typical inhibition and acceleration effects of additives. With potentiostatic electrolysis at potentials from 100 to −400 mV vs. Ag | AgCl | 3.33 mol l^{-1} KCl, the currents drop to constant values within 3 min because of adsorption and complex formation of additives. Accordingly, all the currents were measured at least 3 min after starting electrolysis. The RDE was rotated at speeds of 150, 500, and 1500 rpm.

Table 1
Bath composition

Basic bath	
$CuSo_4 \cdot 5H_2O$ (mol l^{-1})	0.6
H_2SO_4 (mol l^{-1})	1.85
Additive	
NaCl (ppm)	100
PEG (molar masses: 200, 700, and 20 000) (ppm)	400
JGB (ppm)	10
SPS (ppm)	1, 5, 10, 20

The through-mask cathodes to simulate via bottoms were used to monitor the acceleration effect. We formed photoresist patterns on copper foil. The patterns consisted of 30-μm wide lines of exposed copper foil surface and photoresist heights of 10, 30, and 100 μm. The pattern had 10 lines of 16 mm length and 1.0 mm pitch. The photoresist THB-430N (JSR Co.) was used. For 10 and 30 μm resist heights, the patterns were formed by photolithography. The 100-μm height resist was patterned by an Excimer (KRF) laser with an energy density of 1.0 J cm^{-2}. The photoresist patterns were attached to RDE. The electrodeposits were prepared by constant voltage electrolysis at −300 mV vs. Ag | AgCl | 3.33 mol l^{-1} KCl, without rotating RDE.

The deposit cross sections were observed as having a 30 μm width and 30 μm height resist pattern. This pattern has already been shown in Ref. [7]. The electrodeposits were prepared by electrolysis at −300 mV vs. Ag | AgCl | 3.33 mol l^{-1} KCl without rotating RDE. 100, 200, and 400 C were applied. The deposits were then imbedded into epoxy resin and cut perpendicular to the copper surface and polished to obtain the cross sections. These cross sections were observed by optical microscopy.

3. Results

3.1. Current–voltage curves with additives

Fig. 1 shows the current–voltage curves without additive or with the different additives, Cl^-+PEG+SPS, Cl^-+PEG+JGB, and Cl^-+PEG+JGB+SPS. With addition of PEG and Cl^-, all curves shift in the negative direction. This negative shift is considered as an inhibition effect by the additives. With SPS added to

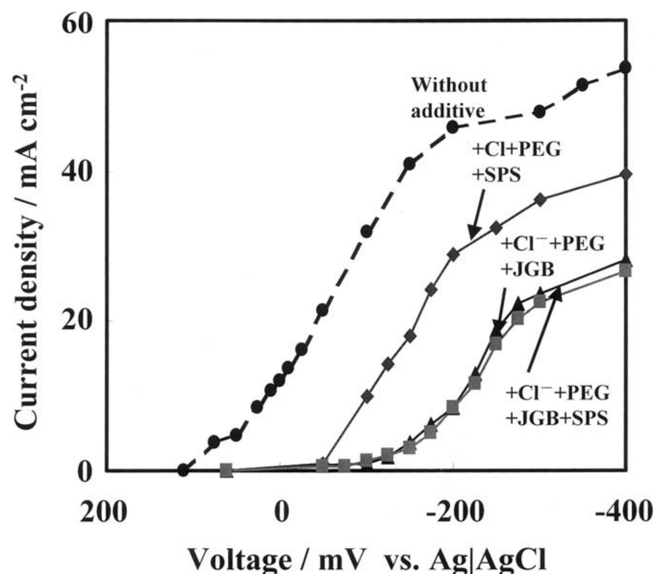


Fig. 1. Effect of super-filling additives on current–voltage curves [8].

PEG and Cl^-, the current increase as compared with Cl^-+PEG+JGB and Cl^-+PEG+JGB+SPS. This is due to the depolarizing effect of SPS. This depolarizing effect is considered as an acceleration effect by the additives.

With SPS added to PEG, Cl^- and JGB, which is a typical combination of the four additives used for super via filling, however, the current does not increase. The curves with Cl^-+PEG+JGB+SPS and Cl^-+PEG+JGB are almost identical. SPS, in this case, does not seem to show the depolarizing effect. These current–voltage curves correspond to the results obtained by Kelly et al. [3–5].

3.2. Inhibition effect by additives

Fig. 2(a) and (b) shows the current–voltage curves with different rotation speeds of RDE of 150, 500, and 1500 rpm. The additives are Cl^-, PEG, and JGB. With Cl^- and PEG in (a), the current voltage curves do not shift with the rotation speed of the RDE. With JGB in addition to Cl^- and PEG in (b), the curves shift negatively with an increase in rotation speed of RDE to 500 and 1500 rpm. This negative shift with rotation speed means that the additives become under diffusion control. The inhibition effect increases with the rotation speed of RDE.

The adsorption of the 30 nm diameter PEG molecules causes this inhibition effect (Fig. 3).[1] The PEG molecules adsorb preferentially at the sidewalls of macrosteps of the copper electrodeposit (Fig. 3, arrow) and inhibit the lateral growth of the macrosteps (5, 7, 8). In the presence of JGB, the PEG molecules become under diffusion control. Outside the via, many PEG molecules are absorbed. The via bottom has a longer diffusion length than the via surface outside. Because of the longer diffusion length, almost no PEG molecules can be observed at the via bottom. This causes the inhibition effect at the via surface and the electrodeposit preferentially fills the via bottom. This is one aspect of a super via filling mechanism and this mechanism is based on the inhibition effect.

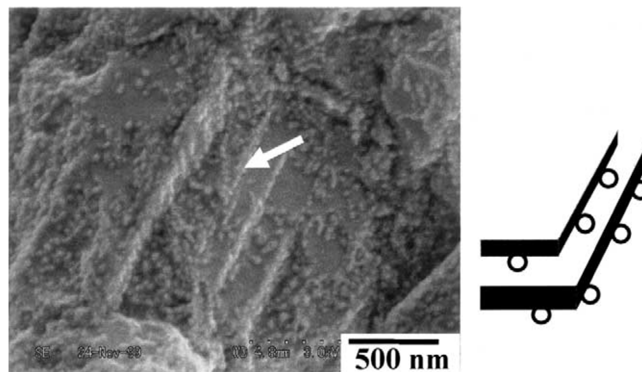


Fig. 3. Field-emission SEM micrograph of the deposit. Additives are Cl^-+PEG [8].

[1] Approximately, 30 nm diameter particles have been identified as the PEG molecules adsorbed because of the following reasons. 7500 molar mass PEG has been used in this work. If 1000 molar mass PEG is used instead, the particle diameter shrinks to 10 nm. The electrodeposits formed with PEG and without PEG-containing electrolyte were removed from the substrate. The element compositions were analyzed by the combustion method. Ten times more carbon and three times more oxygen were detected in the electrodeposit formed with PEG-containing electrolyte.

3.3. Acceleration effect by additives

We used through-mask cathodes to simulate via bottom in order to investigate the acceleration effect (see Fig. 4(b)). The current–voltage curves on a conventional flat-plate cathode have already been reported in Fig. 1. Fig. 4 shows a comparison of the additive effect on the current–voltage curves of this through-mask cathode (b) and a flat-plate cathode (a). The additives are Cl^-+PEG+SPS, Cl^-+PEG+JGB, and Cl^-+PEG+JGB+SPS. As has already been

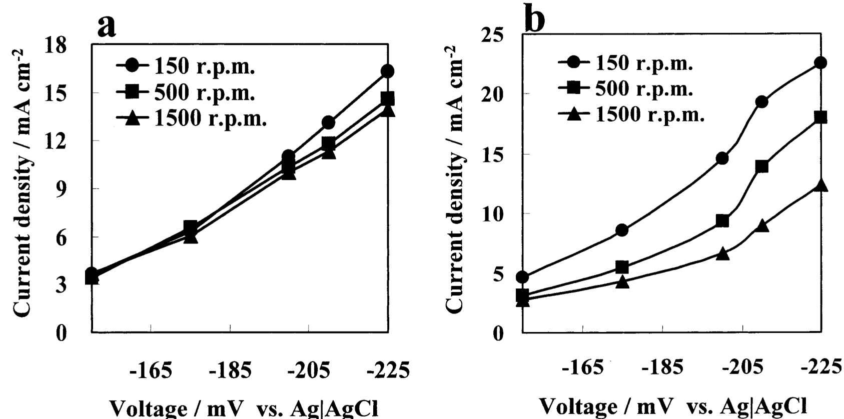


Fig. 2. Effect of rotating disk speed on current–voltage curves with different additives. Additives are Cl^-+PEG+JGB [8]. (a) Cl^- and PEG, and (b) Cl^-, PEG, and JGB.

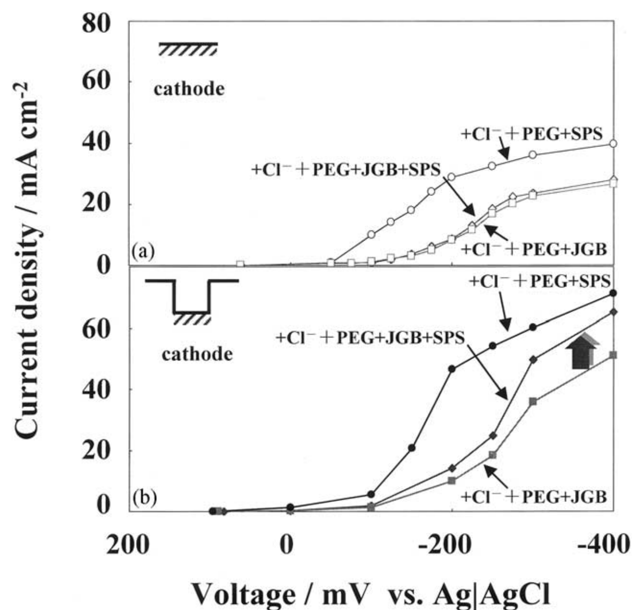


Fig. 4. Current–voltage curves of a flat-plate cathode and a through-mask cathode. (a) Flat-plate cathode, and (b) through-mask cathode to simulate via bottom.

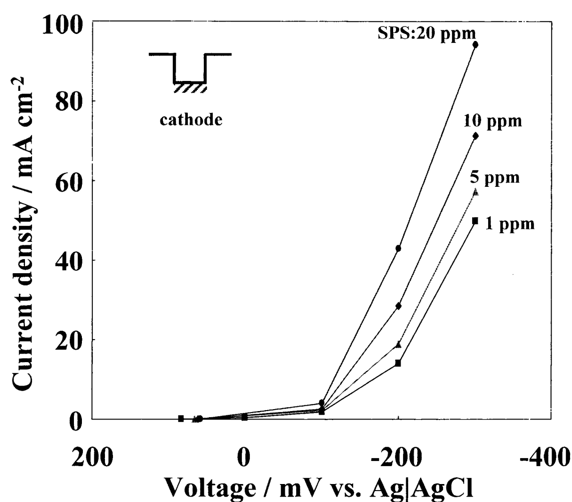


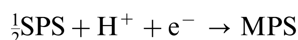
Fig. 5. Current–voltage curves with different SPS concentrations. Additives are Cl^- +PEG+JGB+SPS.

shown in Fig. 1, the current–voltage curves with Cl^- + PEG+JGB and Cl^- +PEG+JGB+SPS are almost identical for the flat-plate cathode (Fig. 4(a)). With a through-mask cathode, these current–voltage curves are different (Fig. 4(b); see arrow). The current increases with Cl^- +PEG+JGB+SPS as compared with Cl^- + PEG+JGB. This is because of the through-mask cathode. With a through-mask cathode, we succeeded in obtaining the depolarizing effect of SPS with a typical combination of the four additives used for super via filling.

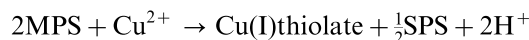
Fig. 5 shows the current–voltage curves of through-mask cathode with additives of Cl^- +PEG+JGB+ SPS. The SPS concentrations have been increased from 1, 5, 10 to 20 ppm. The current increases with an increase in SPS concentration. We can conclude that SPS has via bottom depolarizing effect even with four additives of super via filling.

Fig. 6 shows the current–voltage curves of different aspect ratio through-mask cathodes with additives of Cl^- +PEG+JGB+SPS. The aspect ratios are 0.33, 1.00, and 3.33. The cathode width was fixed as 30 μm and the resist height was varied as 10, 30, and 100 μm. The SPS concentrations were 10 and 20 ppm. The current increases with an increase in aspect ratio of the through-mask cathode. The current increases with a higher aspect ratio both for 10 and 20 ppm SPS concentrations.

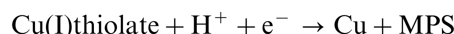
Farandon et al. [2] proposed cuprous thiolate (MPS) complex formation during the copper electrodeposition.



$$\tfrac{1}{2}\mathrm{SPS} + \mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{MPS}$$



$$2\mathrm{MPS} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Cu(I)thiolate} + \tfrac{1}{2}\mathrm{SPS} + 2\mathrm{H}^+$$



$$\mathrm{Cu(I)thiolate} + \mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{Cu} + \mathrm{MPS}$$

Since the current increases with an increase in SPS concentration (Fig. 5), the Cu(I)thiolate complex must be an accelerator and must accumulate at the via bottom cathodes. The complex remains at the via bottom for deeper vias of higher aspect ratios. The complex escapes easily from the via bottom with a lower aspect ratio of 0.33. This remains at the via bottom and accelerates the current at a via bottom cathode of the higher aspect ratio of 3.33.

Fig. 7 shows the cross section of via filling with electrodeposit. The via has an aspect ratio of 1.0 and a 30 μm bottom length and 30 μm resist height. A typical combination of four additives, Cl^- +PEG+JGB+SPS, has been used. The charge was changed from 100 C (initial stage), 200 C (middle stage), and 400 C (final

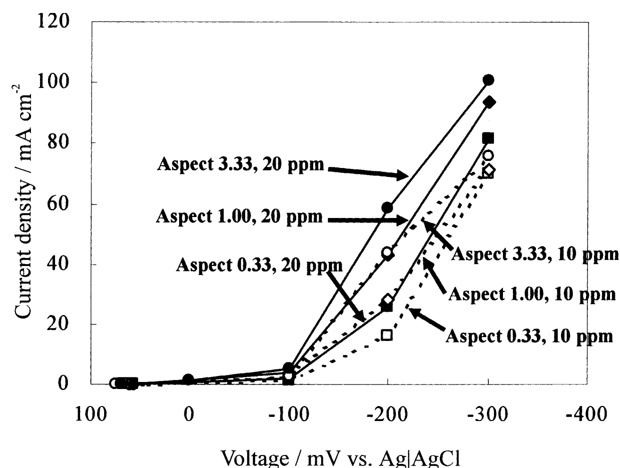


Fig. 6. Effect of aspect ratio of current–voltage curves. Additives are Cl^- +PEG+JGB+SPS.

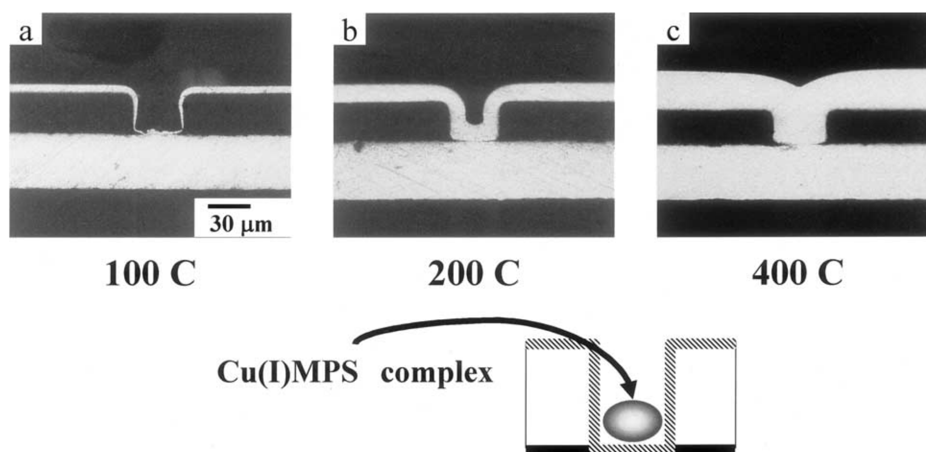


Fig. 7. Cross-sectional view of electrodeposit into via: (a)100 C, (b)200 C, and (c)400 C.

stage). The lower white portion is the 30 μm thickness copper foil and the via is at the center of the copper foil. The 30 μm thickness photoresists are on both the left and right hand sides of the via. The copper electrodeposit is on the upper surfaces, the sidewalls of the photoresists, and also on the copper foil via bottom.

For the initial stage (100 C) of via filling, the deposit thickness at the via bottom (see arrow in Fig. 7(a)) is much thinner than that outside the via on the photoresist upper surfaces. For 200 C, the via bottom thickness increases and the thickness is same at both the via bottom and outside the via. For the final stage of 400 C, the via bottom thickness increases drastically and the via is filled completely. The via bottom thickness is thinner at the initial stage and this thickness increases with charge. The above-mentioned accelerator which is related to SPS does not accelerate the via bottom current at the initial stage of electrodeposition. This SPS substance starts to accelerate the current from the middle stage of electrodeposition at 200 C. The via bottom accelerating complex must form during the electrolysis and accumulate at the bottom of the deeper vias.

The increase in deposit thickness at the via bottom in the course of time holds also for the 0.3 μm width via used for the copper damascene process. Cross-sectional SEM micrographs and numerical simulation were reported by West et al. [12].

4. Conclusions

The role of via filling additives was investigated by a through-mask cathode to simulate via bottoms. The results are summarized as follows:

1) Current–voltage curves were measured with a through-mask cathode. The current increases with additives of Cl^- + PEG + JGB + SPS compared with Cl^- + PEG + JGB. The current also increases with an increase in SPS concentration. A depolarizing effect of SPS was found with the typical combination of four additives (Cl^- + PEG + JGB + SPS) used for via filling.
2) The current increases with an increase in aspect ratio of the through-mask cathode. With the higher aspect ratio of a deeper via, the via bottom accelerating Cu(I)thiolate complex must accumulate at the via bottom.
3) At the initial stage of via filling, the deposit thickness at the via bottom is thinner than that at the via outside. The thickness becomes the same for both the via bottom and outside the via at the middle stage. The via bottom thickness increases drastically at the final stage. The via bottom accelerating complex must form during the electrolysis. This accumulates at the via bottoms of deeper vias.

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