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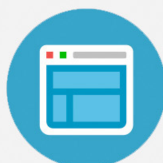

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Wetting effect on gap filling submicron damascene by an electrolyte free of levelers

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By using an acid–copper electrolyte without levelers and brighteners, we achieved defect-free filling of 0.13 μm vias with aspect ratio 8:1. This novel electrolyte consisted of copper sulfate ($CuSO_4 \cdot 5H_2O$), sulfuric acid (H_2SO_4), chloride ions (Cl^-), and two different average molecular weights of polyethylene glycols (PEG). The smaller-molecular-weight PEG200, with higher diffusion ability, was identified to enhance cupric ions transporting into deep features and was treated as a bottom-up filling promoter. The larger-molecular-weight PEG2000, with higher polarization resistance, provided enough inhibition effect on cupric ion reduction to obtain denser and small-grained deposits in a lower-current-density region, which benefits the filling capability in submicron features. In addition, adding PEG2000 could reduce the interfacial energy between the electrolyte and the opening of trenches/vias to enhance the filling capability. © *2002 American Vacuum Society.* [DOI: 10.1116/1.1486231]

I. INTRODUCTION

To overcome the challenge of copper electroplating in a narrow structure, an effective electrolyte must simultaneously provide lower surface tension, sufficient activation over potential, and selective inhibition gradient within the features.[1,2] Until now, electrolytes have usually contained carrying agents and levelers. In general, adding a carrying agent reduces the surface tension of the electrolyte, making it easier to transport into deep gaps. Carrying agents are also referred to as wetting agents.[3] They are polyethers, typically polyglycols, which are random copolymers of ethylene oxide; or propylene oxide with a molecular weight in the range of 5000–15 000. However, improving the necessary activation over potential and selective inhibition gradient within the feature could be implemented by adding effective levelers to plating baths. In our previous study,[2] we demonstrated that 2-mercaptopyridine (2-MP) was an effective leveler for filling 0.13 μm vias. Moreover, in other studies,[4,5] Kelly and co-workers showed the leveling of 0.2 μm trenches by an acid–copper electrolyte with polyethylene glycol (PEG), Cl^-, bis (3-sulfopropyl) disulfide, and Janus Green B. Even at a scale down to sub-0.15 μm, defect-free filling phenomena were obtained through the proper assembly of wetting agents and levelers. The leveling abilities, especially those of levelers or brighteners such as polyamines, or heterocyclic compounds containing S and N atoms, have been verified by many research groups.[4–9] However, those levelers and brighteners adsorb on the electrode surface and then react with the metallic copper, creating a relatively brittle and high-resistivity deposit by forming copper sulfide (CuS).[10]

Although there are many levelers without such drawbacks, the rigid requirement of high-anisotropic deposition issued from ultranarrow and deep structures limits the range of choice of alternative levelers. If the concise adjustment of wetting agents in electrolytes could achieve superfilling properties, the design tolerance of other additive parameters, such as species of levelers or their concentrations, could be relaxed. Additionally, integral issues such as electrical characteristics would obtain wider process windows. In this study, we achieved superfilling performance in 0.13 μm vias with aspect ratio 8:1 by using an acid–copper electrolyte without leveling agents and brighteners. The electrolyte only included two different average molecular weights of polyethylene glycol as wetting agents: one has a lower molecular weight with a degree of polymerization (DP) of 200, and the other has a higher molecular weight with a DP of 2000. This novel scheme for solving gap-filling issues by a moderate combination of wetting agents is unprecedented. Concurrently, the film resistivity was reduced because this novel

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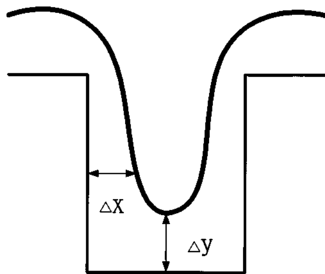

FIG. 1. $\Delta y/\Delta x$ ratio is taken as the characteristic to measure the filling capability.

electrolyte does not include additives that contain S and N atoms. In this text, we propose a model that explains the bottom-up filling mechanism of these assembled wetting agents. Furthermore, we found that the quality of the film deposited in the lower-current-density range apparently improved by adding PEGs in the electrolyte. This effect of PEGs was very important for gap-filling submicron patterns because the higher-filling capability operated in the lower-current-density region.

II. EXPERIMENT

In this study, the blanket wafer was prepared by depositing a 50 nm sputtered TaN diffusion barrier and a 50 nm sputtered copper conduction layer on a SiO_2/Si substrate. The patterned wafer was composed of a 30-nm-thick chemical-vapor deposition Ti/TiN layer as the diffusion barrier and a 200-nm-thick ionized-metal plasma Cu film as the seed layer. In copper electroplating processes, the standard electrolytes were composed of $CuSO_4 \cdot 5H_2O$ (30 g/l), H_2SO_4 (275 g/l), and chloride ions (50–100 ppm). All electroplating work proceeded at room temperature. Potentiodynamic polarization was used to analyze the attribution of additives in acid–copper electrolytes. We performed this polarization with an EG&G potentiostat/galvanostat model 273A. The counter electrode was platinum. The working electrode was copper with constant surface area of 0.5 cm^2. The scanning rate was 2 mV/s and the condition time was 120 s. The initial potential started at +100 mV. The final potential was completed at −1.0 V from the open-circuit potential. All potentials were reported relative to the Ag/AgCl electrode, which served as the reference electrode. Additionally, the cross-section profiles and the thickness of the deposited films were examined by using field-emission scanning-electron microscopy (SEM). The sheet resistance of the copper deposits was measured by the four-point-probe technique. The resistivity measurements were carried out immediately after deposition. The surface tension measurement of the plating solution was examined using a Kruss model K90. In this study, we calculated the filling ratio $\Delta y/\Delta x$ of "bottom-up" to "sidewall shift" from the cross section of a partially filled copper profile on the SEM photograph to define the filling power of copper electroplating, as shown in Fig. 1.[2]

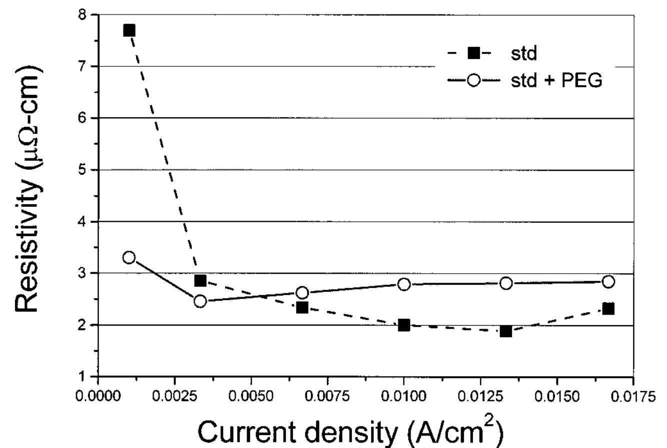

FIG. 2. Resistivity of copper deposits vs supplied currents.

III. RESULTS AND DISCUSSION

In ultra-large-scale-integrated technologies, modern electrolyte baths for copper metallization processes contain several ingredients that are added in small quantities to produce various desirable material properties and filling capabilities. Typically, polyethylene glycol is adopted as a carrying agent in copper electroplating[11] and can improve wetting ability between the electrolyte and copper surface. (In our experiments, the average contact angle of the standard electrolyte with PEG2000 was 13.79°. Without PEG2000 the average contact angle was 19.46°.) Although the acid–copper electrolyte free of PEG could wet the deposited surface, this electrolyte provided neither enough of a suppression effect to produce a smoother film nor enough of a lower surface tension to overcome the capillaceous phenomena of a deep gap (the surface tension γ of the additive-free electrolyte was about 73.38 mN/m; the surface tension of the electrolyte with PEG2000 was about 47.57 mN/m). Figure 2 shows that by adding PEG2000 to the electrolyte, a lower-resistivity film could be obtained in a lower-current-density region. This result is because the electrolyte with PEG2000 could produce a higher polarization resistance than the electrolyte without PEG2000 in the lower-current-density region, inhibiting cupric ion reduction, as shown in Fig. 3. An increase of the polarization effect enhanced the copper nucleation process, which promoted the formation of smoother copper film and gave uniform grain distribution, resulting in a lower-resistivity copper film.[12] Kelly and West[11] demonstrated that the combined action of Cl–PEG on an acid–copper electrolyte inhibits the deposition reaction for cathodic over potentials of up to about 150 mV. Only adding Cl^- promoted the deposition reaction, whereas only adding PEG had a relatively small effect on electrode kinetics. In contrast, in aspects of the gap-filling capability of electrodeposition in vias and trenches, in the lower-current-density region the operation condition for excellent filling capability was found, as can be seen in Fig. 4. An excess of supplied current caused severe copper aggregation and nonuniform current distribution.[12,13] Finally, at the shoulder of vias/trenches, the deposition rate was too high to get complete filling. Although

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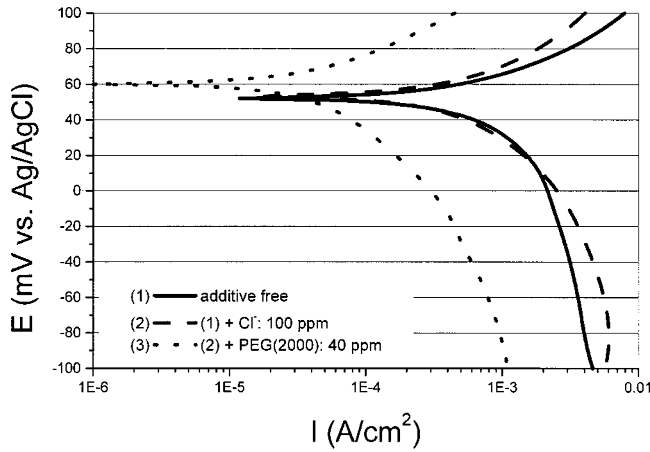

FIG. 3. Potentiodynamic polarization curves of various electrolytes.

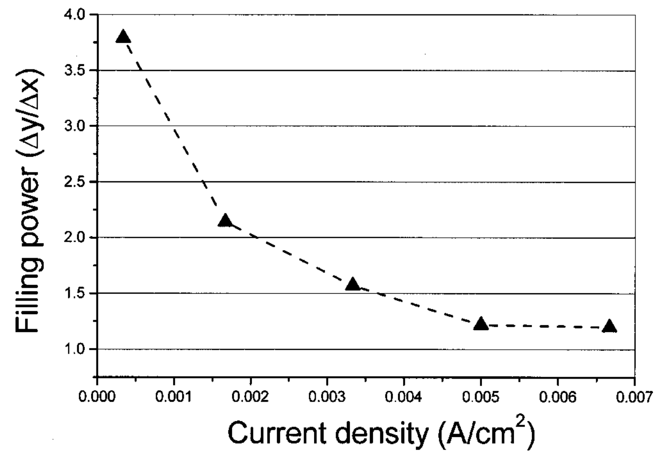

FIG. 4. For 1 μm trenches, filling power $(\Delta y/\Delta x)$ vs different applied currents.

different cupric ion and sulfuric acid concentrations will alter the plating current density in the practical process, adding PEG benefits copper electroplating because higher filling capability and lower film resistivity can be obtained simultaneously in the lower-current-density region. In Fig. 5(a), we see that the electrolyte without PEG produced a rougher film and voids.

In agreement with previous reports of the chemistries used to demonstrate superfilling in submicron dimensions, many groups have published reports recently describing the combined effect of C1–PEG and other filling promoters in achieving sub-0.2-μm gap filling. Moffat *et al.* have also reported that superconformal electrodeposition of copper in 500-nm-deep trenches ranging from 500 to 90 nm in width was achieved by an acid cupric sulfate electrolyte with the combined action of C1–PEG and 3-mercapto-1-propanesulfonate.[14] Moreover, in our previous study,[2] we demonstrated that Cl–PEG and 2-MP could fill 0.13 μm vias. Although PEG is usually adopted as an important additive in copper electroplating, the applicability would be limited if a single PEG could not simultaneously exercise control of mass transport and grain growth. In this article, we found PEG2000 could reduce the surface tension of the electrolyte and improve the film quality. In contrast, PEG200 could enhance cupric ions transporting into the feature's bottom. The surface tensions (γ) of electrolytes decreased with the increase of molecular weights of the added PEGs in the following order: PEG-free solution (73.38 mN/m)>PEG200 (2000 ppm) (72.83 mN/m)>PEG2000 (40 ppm) and PEG200 (2000 ppm) (51.88 mN/m)>PEG2000 (40 ppm) (47.57 mN/m). The electrolyte with PEG2000 has a lower

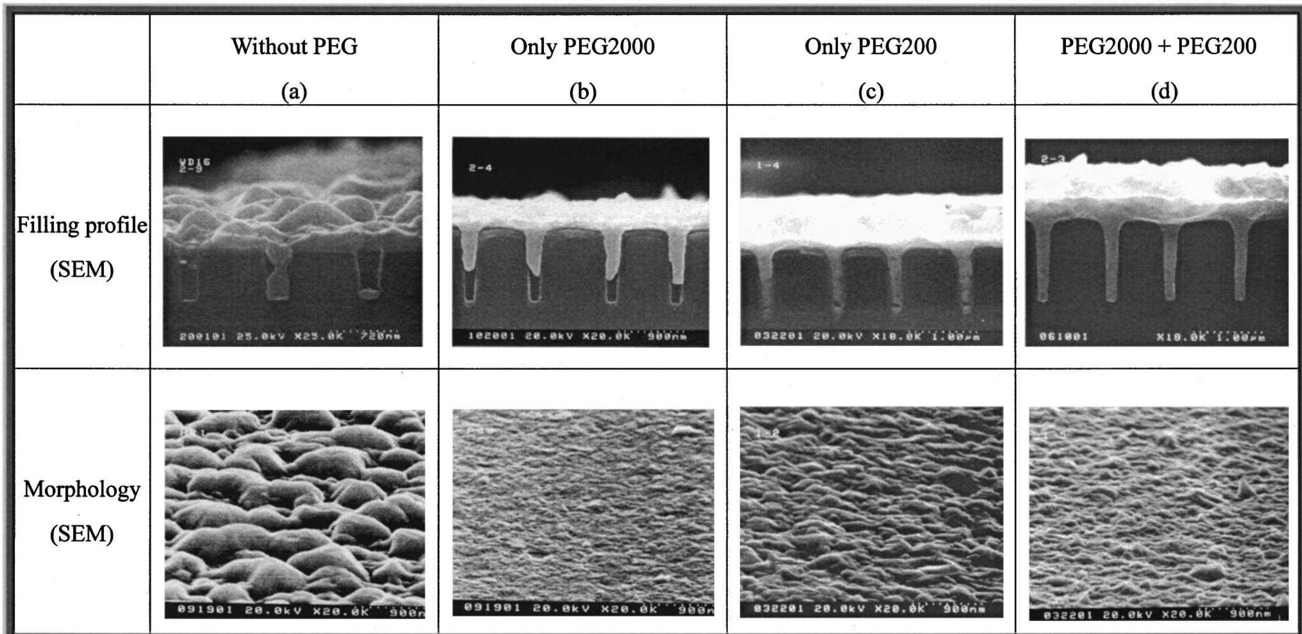

FIG. 5. Effects of PEGs on filling capability and surface morphology: (a) without PEG; (b) only PEG2000; (c) only PEG200; and (d) PEG2000 and PEG200.

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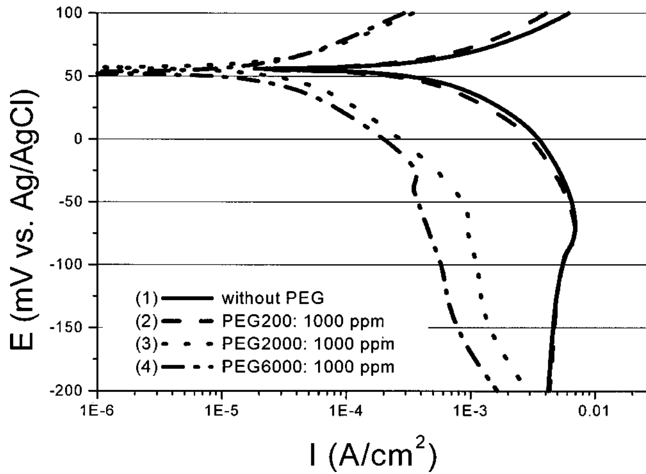

FIG. 6. Potentiodynamic polarization curves of the degree of polymerization of PEGs increased from 200 to 6000.

surface tension than the additive-free solution. The electrolyte with PEG2000 was effective for filling larger and shallower vias. However, when damascene was scaled down gradually or with a higher aspect ratio, the filling capability of the electrolyte with single PEG2000 was worse. Observing Fig. 5(b), the added PEG2000 only carried the electrolyte diffusing into outer portions of the 0.18 μm vias. In Fig. 5(b), we also see that a smoother film was obtained by adding PEG2000 to the electrolyte. This occurred because the added PEG2000 produced a higher polarization resistance to inhibit cupric ion reduction. This effect was considered as a contribution from the stronger adhesion force between higher-molecular-weight PEG2000 and the copper surface through copper complex formations, and the stronger intermolecular forces between the PEG molecules. Reid and David[15] examined PEGs in the molecular-weight range of 200–20 000. Reid and David found an apparent effect on potential shift in the high-molecular-weight fractions of PEGs. In our work, we also observed an increase of "Tafel slope" of an acid–copper bath, while as can be seen in Fig. 6, the degree of polymerization of PEGs increased from 200 to 6000.

To increase the probabilities of interactions between electrolytes with deposited substrates, the contact angle between electrolytes and substrates must be as low as possible. In other words, the surface tension of the electrolyte should be kept low. Hence, the cupric ion flux of the electrolyte with PEG2000 should be higher than the electrolyte with PEG200 at the bottom of the features. However, Fig. 5(c) shows a higher flux of cupric ions at the deeper region of the same feature (0.18 μm vias) for the electrolyte with only PEG200. The poor wetting effect of PEG2000 in the deep gap was an interesting observation. One proposed explanation is illustrated in Fig. 7. We suggest that a wetting profile in the tube-type via was determined by interfacial energies among three phases. In Fig. 7, the electrolyte with PEG2000 and its lower surface tension obtained a smaller angle (13.79°) between the copper seed surface and the liquid phase. This result implies that the penetration depth of the electrolyte along the sidewall of the damascene was deeper than that of the electrolyte with the smaller-molecular-weight PEG200 (with a larger contact angle of 17.6°). This conclusion was the same as the conclusion about the wetting effect on a normal blanket surface. For the damascene structures, the wetting effect near the central region of the damascene pattern was different from the wetting effect on blanket surfaces or larger gaps. The meniscoid curvature for the liquid-gas front plane of the electrolyte with PEG200 was smaller than that of the electrolyte with PEG2000; therefore, PEG200 could carry the electrolyte into the damascene more uniformly than PEG2000. Furthermore, the possibility of forming voids at the lower portion of the feature for the electrolyte with PEG200 was lower than the condition for the electrolyte with PEG2000. Although adding only PEG200 to the electrolyte could enhance cupric ions flowing into deeper

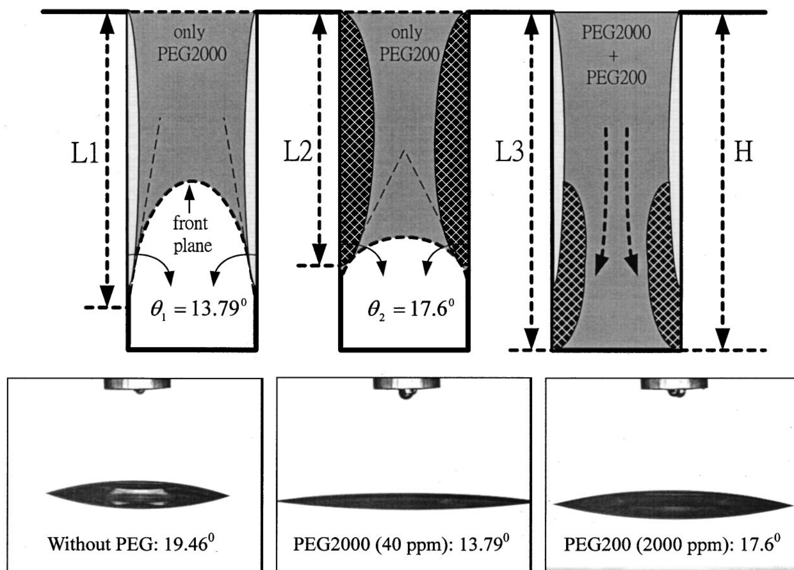

FIG. 7. Proposed diagram of the wetting effect by the electrolyte with PEG200 or PEG2000 within the feature.

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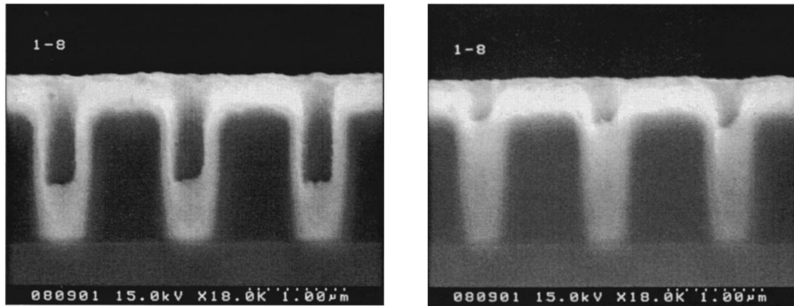

FIG. 8. Bottom-up filling transient mechanism of the electrolyte with PEG2000 and PEG200.

regions of damascenes, the added PEG200 with a higher surface tension did not penetrate as deeply as the electrolyte with PEG2000. Additionally, to overcome the capillary force of the small gap, the surface tension of the electrolyte should be below a threshold value. This factor is the reason why the additive-free electrolyte without PEG flows with difficulty into the deeper gaps, as shown in Fig. 5(a). Moreover, as reported by Shimizu and Kenndler,[16] the added PEG200 could facilitate cupric ions transporting into inner portions of deep trenches/vias because of its higher diffusion ability. This feature was collocated with the higher concentration of PEG200 in the plating bath (1500–2000 ppm), forming a uniform concentration distribution within the damascene. This advantage for PEG200 maintained a more regular electroplating reaction in the entire damascene and was treated as a bottom-up filling promoter. However, a rougher deposit was produced because its polarization resistance was lower than PEG2000. In our work, adding only PEG2000 did not achieve the defect-free filling in sub-0.35-μm vias in the range of concentration from 40 to 2500 ppm. However, until the concentration reached 500 ppm, PEG200 was not valid for improving the surface roughness and the filling capability.

Figure 6 shows polarization measurements with the degree of polymerization of PEGs increased from 200 to 6000. We see that when the applied current density is 0.001 A/cm^2, the activation over potential is 142.32 mV for the case of PEG2000 (1000 ppm) and is 23.17 mV for PEG200 (1000 ppm). Based on these data, we can deduce that PEG2000 forms a higher barrier or stronger inhibition effect during electroplating than PEG200. To force the electrolyte to be pulled into sub-0.2-μm trenches/vias and improve the quality of electroplated copper, we added two different molecular weights of PEGs to the plating bath. In Fig. 5(d), the SEM image shows that the defect-free profiles of 0.13 μm vias with aspect ratio of 8:1 were deposited by fine-tuned concentrations of both PEG2000 and PEG200. We see that defects and voids disappear in deep features and that the quality of copper deposits in vias was improved. In the electroplating process, the smaller-molecular-weight PEG200, with higher-diffusion ability, enhanced the flux of cupric ions within the deep feature. Furthermore, the larger-molecular-weight PEG2000 reduced the surface tension of the electrolyte and improved the uniformity of the deposited films. Figure 8 displays the bottom-up filling transient mechanism of this novel electrolyte. In our detailed analyses of concentration ranges of wetting agents for achieving a superfilling in sub-0.13-μm features, the ranges were 40–120 ppm for PEG2000 and 1500–2000 ppm for PEG200. If the levelers or brighteners (10–100 ppm) were also added in the electrolyte, the ranges were expanded to be 20–200 ppm for PEG2000 and 500–4000 ppm for PEG200. In general, levelers and brighteners were the major contributors affecting the resistivity of copper deposits.[10] The added PEG, producing a finer-grain structure, apparently does not increase the resistivity of copper films. The resistivity of the deposited copper film for the case without levelers and brighteners was as low as 2.6 $\mu\Omega$ cm, as compared with 8.62 $\mu\Omega$ cm for another case using 2-mercaptopyridine as the gap-filling promoter.

IV. CONCLUSIONS

In this study, we found that the added PEG2000 benefited copper electroplating because the higher filling capability and the lower copper resistivity could be obtained simultaneously in the lower-current-density region. Furthermore, the limitation of filling narrower and deeper gaps could be overcome by the electrolyte with PEG2000, which reduces the surface tension of the electrolyte and provides grain growth control, and with PEG200, which enhances cupric ions transporting into deeper regions. The bottom-up filling phenomenon of this novel electrolyte with different functions of PEGs was explained by an experiment-based model. The electrolyte with this arrangement achieved a defect-free filling in 0.13 μm vias without the aid of levelers and brighteners. The resistivity of copper films deposited by this novel electrolyte was as low as 2.6 $\mu\Omega$ cm, as compared with 8.62 $\mu\Omega$ cm for another case using 2-mercaptopyridine as the gap-filling promoter.

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