

## Investigations of effects of bias polarization and chemical parameters on morphology and filling capability of 130 nm damascene electroplated copper

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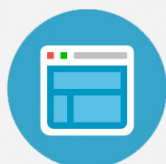
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# Investigations of effects of bias polarization and chemical parameters on morphology and filling capability of 130 nm damascene electroplated copper

Shih-Chieh Chang, Jia-Min Shieh,<sup>a),b)</sup> Kun-Cheng Lin, Bau-Tong Dai,<sup>a)</sup> Ting-Chun Wang, Chia-Fu Chen, and Ming-Shiann Feng

*Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan*

Ying-Hao Li and Chih-Peng Lu

*Merck-Kanto Advanced Chemicals Limited, Taipei, Taiwan*

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Through elucidating the effects of current density, cupric ion concentration, bath temperature, and air agitation on plating uniformity and filling capability of copper electroplating, the deposition of copper in an acid copper electrolyte will be illustrated to scale down to the sub-0.13  $\mu\text{m}$  features with uniform plating, which is required by chemical mechanical polishing in current damascene techniques. In order to achieve the defect-free filling in sub-0.13  $\mu\text{m}$  vias and trenches, the electrolyte must be composed of proper amounts of cupric ions, sulfuric acid, chloride ions, wetting agent, and filling promoter. The supplied current controlled at a lower current density, agitation acceded to the electroplating process were found as further keys. In the electrolyte, the filling promoter was consisted essentially of thiazole derivatives with benzyl groups and amino-group ( $-\text{NH}_2$ ) offering sufficient inhibition on copper depositing and selective inhibition gradient. Moreover, a lower resistivity film and higher filling capability could be obtained by using periodic pulse current plating as compared with direct current plating. © 2001 American Vacuum Society. [DOI: 10.1116/1.1368673]

## I. INTRODUCTION

Electroplating technology has already been the promising method for depositing copper films onto patterned dielectrics for ultra scale integrated (ULSI) interconnect fabrication.<sup>1-4</sup> As the damascene process procedure, the copper is first filled into previously etched holes and trenches in insulators and then planarized by chemical mechanical polishing (CMP). One of the challenges of copper electroplating is the typically nonuniform deposit arising from variations in potential and in cupric ion concentration over the plating metal surface.<sup>5,6</sup> When cupric ions are reduced in vias or trenches, these variations can lead the formation of voids in the plated gaps.<sup>7</sup> Such voids will degrade the conductance and electromigration resistance of copper lines. In addition, the trapped electrolyte can destroy circuit performance and result in a contamination, corrosion, and reliability risk.<sup>8</sup>

In traditional printed circuit board (PCB) application, copper is plated into large dimension through holes, the effects of convection, diffusion, electrolyte composition, and solution resistance are all important in determining the uniformity of the plated deposit.<sup>8</sup> In ULSI technology, the feature scale is diminished to submicron, the plating nonuniformity became as a consequence in term of diffusion limitation alone.<sup>7,8</sup> In our previous work about the investigation of gap-filling dynamics, the electrolyte obeying the adsorption-diffusion dynamics must simultaneously provide lower surface tension, sufficient inhibition on copper depositing and

selective inhibition gradient within the feature.<sup>9,10</sup> In general, adding a wetting agent can decrease surface tension between the electrolyte and the electrode. The surface tension was also related to diffusion rate of wetting agent. So far, the diffusion behavior of electrolyte simultaneously influences the morphology and filling capability of the damascene pattern. Mapping to real electroplating system, both the bath temperature and rotation of the cathode are two major factors influencing the diffusion mechanism of the electrolyte excepting their intrinsic chemical characteristics. One research group mentioned that there existed a range of operation temperature for achieving damascene gap-filling quality.<sup>11</sup> If considering that in a more macrocosmic sense, all of the chemical recipe and mechanical, electrical parameters would influence those interested topics. In fact, the effects of those separate parameters on diffusion mechanisms would respond to the over potential of electroplating system. The approximate mathematical analysis derived by Fick's first law could explain those dynamics in excess of macroscale. Therefore, in this study, the effects of current density, cupric ion concentration, bath temperature, and air agitation on plating uniformity of copper deposits will be discussed in detail. These results will fit the CMP requirement and achieve the defect-free filling in submicron damascene. Furthermore, the proper control of plating condition will decrease the requirement of additives and improve the electrical performance of copper lines. In order to overstrike threshold of an abruptly increasing gap-filling challenge in sub-0.13  $\mu\text{m}$  damascene features, adding seed-layer-enhanced chemistries into the electrolyte is also necessary. The recipe of the composition and concentration of electrolyte for sub-0.13  $\mu\text{m}$  copper metallization

<sup>a)</sup>Also at National Nano Device Laboratories, Hsinchu 30050, Taiwan.

<sup>b)</sup>Author to whom all correspondence should be addressed; electronic mail: jmshieh@ndl.gov.tw

application was optimized with the aid of pulse bias current wave form and concise current level.

## II. EXPERIMENT

Our copper electroplating experiments were carried out in Hull Cell.<sup>12</sup> Agitation air was introduced into the solution from a compressor. The sample size utilized in this work was  $1 \times 3 \text{ cm}^2$ . The blanket wafer for this study was prepared by depositing a 50 nm sputtered TaN diffusion barrier and a 50 nm sputtered Cu conduction layer on a  $\text{SiO}_2$ . 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 gap-filling experiment, the electrolyte was composed of copper sulfate (30 g/l), sulfuric acid (275 g/l), chloride ion (100 ppm), wetting agent (20–2000 ppm), and filling promoter (10–200 ppm). The sheet resistance of copper deposit was examined by four-point probe measurement. On the other hand, the thickness and cross section profile of deposit film were analyzed by field emission scanning electron microscope (FESEM) and surface roughness was measured by an atomic force microscope (AFM), of DI Nanoscope.

## III. RESULTS AND DISCUSSION

### A. Polarization effects on surface morphology

Generally, electroplating metal deposits with fine-grained structure, and uniformly distributed metal layer can usually be obtained from the process electrolytes that are capable of being operated at larger over potential.<sup>13</sup> According to the principles of electrocrystallization, the rate of formation of new nuclei on the electrode surface increases exponentially as the cathodic polarization  $\eta$  increases:<sup>13,14</sup>

$$\omega = B \exp\left(-\frac{K}{\eta^2}\right), \quad (1)$$

where the constants  $B$  and  $K$  are specific for a given metal and temperature. If all other factors remain constant, the increase of cathodic polarization will result in a larger number of newly formed nuclei and a finer-grained structure of the deposits. When an electroplating process occurs at an electrode, its potential changing from the equilibrium potential (often called steady state) is called polarization. The over potential caused by polarization in an electroplating process can be due to the activation, concentration, and ohmic polarization.<sup>13–16</sup>

In general, a metal electroplating reaction will tend towards mass transport control because of the rate of reactant supply is slow in comparison with the rate of electron transfer at the electrode surface.<sup>8,15</sup> Assuming that discharged ions are replenished only by diffusion (if migration is negligible), then, the application of current  $i$  has produced concentration over potential of

$$\eta'_c = \frac{RT}{zF} \ln\left(1 - \frac{i}{i_L}\right). \quad (2)$$

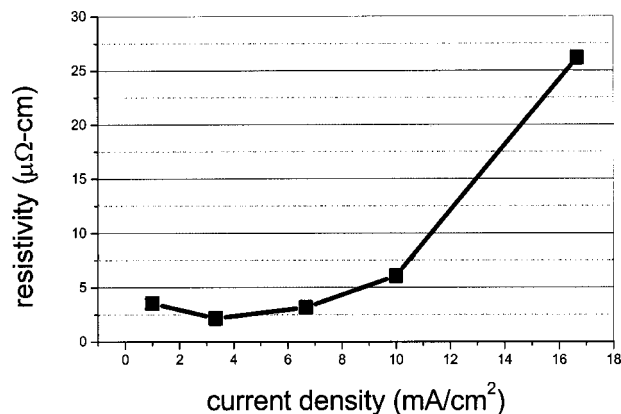


FIG. 1. Resistivity of copper deposits vs applied current densities; the electrolyte was composed of copper sulfate (30 g/l) and sulfuric acid (275 g/l).

This equation is typically employed whenever the diffusion species is the potential-determining ion. Furthermore, according to Faraday's law and Fick's first law, the limiting current,  $i_L$  could be expressed as

$$i_L = \frac{A_z F D C_b}{\delta_N}, \quad (3)$$

where  $A$  is the area of cathode,  $F$  is Faraday's constant,  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $z$  is the charge of the cation,  $\delta_N$  is the thickness of diffusion layer, and  $C_b$  is bulk concentration.

According to Eqs. (1) and (2), we could see that when the applied current density increases toward the limiting current density  $i_L$ , the cathodic polarization of the electroplating process increases while resulting in metal deposits with finer-grained structure. Meanwhile, if the higher limiting current density was assigned, the larger process window of the practical applied current is expected.

According to the range of the current density, the electroplating process could be divided into two regions of mechanisms. First, the electrocrystallization process is a charge transfer controlled dominant reaction under lower current density. As the bias current is increased, a mass transfer controlled dominant reaction takes over until limiting current density is reached, finally, the reaction is pure mass transfer controlled. In Fig. 1, we found that in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (30 g/l) and  $\text{H}_2\text{SO}_4$  (275 g/l) containing electrolyte, the resistivity of copper films decreased with increasing applied current until a threshold current was reached, and then the resistivity became larger with increasing the supplied current. This could be understood as that an increase in the current density would enforce the polarization effect and thus enhance the copper nucleation process, which promotes the formation of smoother copper film and gives uniform grain distribution, resulting in a lower resistivity copper film.<sup>8,13</sup> However, when more current was further supplied, the depletion of cupric ions in the diffusion layer near the surface of the cathode would become more severe; therefore, cupric ions were more difficult to be replenished instantly from the solution into the diffusion layer.<sup>17</sup> In addition, since cupric ions

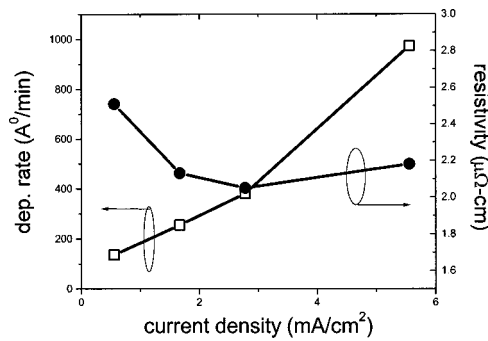


FIG. 2. Resistivity of copper deposits and the deposition rate vs applied current densities in whole sized wafers.

were reduced very fast and Cu aggregation occurred around the protrusion on the surface under higher electric field, the morphology of deposits became spongy or dendritic. Concurrently, less dense packing and high resistivity of deposits were formed at higher current plating. The consistent trend also could be found in whole sized wafer electroplating as shown in Fig. 2. Following the same result observed in Fig. 1, Fig. 3 shows that the surface morphologies of copper deposits became smoother with increasing applied current density until a threshold current density was reached, and then the surface of deposited films became rougher with increasing the applied current density. From the SEM photos in Fig. 4, the copper film deposited at 3.33 mA/cm<sup>2</sup> was smoother than the film deposited at 1 mA/cm<sup>2</sup>. But the morphology became spongy when the applied current density was increased to 6.67 mA/cm<sup>2</sup>. Additionally, higher bath temperature could raise the diffusion coefficient  $D$ ; and the limiting current  $i_L$  becomes larger according to Eq. (3). It means that the polarization effect decreases if the operated current density remains unchanged because the diffusion layer is mitigated at a higher bath temperature. On the other hand, lower temperature slows down the mobility of cupric ions on the plating surface and consequently reduces the chance of consolidating neighboring grains. In Fig. 4, the morphologies of the copper films plated at 50 °C appeared rougher than that

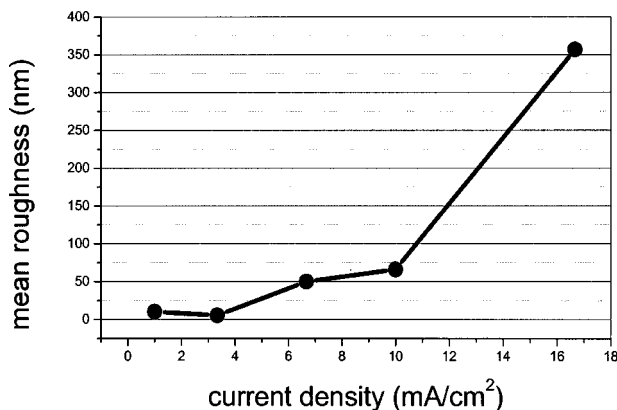


FIG. 3. Mean roughness (Ra) of copper deposits vs applied current densities; the electrolyte was composed of copper sulfate (30 g/l) and sulfuric acid (275 g/l).

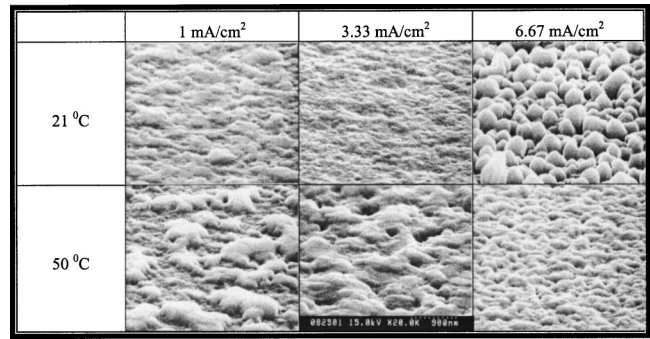


FIG. 4. Surface morphologies of copper films with different applied current densities and the relationship with temperature; the electrolyte contained 30 g/l  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 275 g/l  $\text{H}_2\text{SO}_4$ .

plated at 21 °C even applied current density at 1 or 3.33 mA/cm<sup>2</sup>. Furthermore, at a higher current density of 6.67 mA/cm<sup>2</sup>, the copper deposit plating at 21 °C became spongy but the deposit plated at 50 °C was not. The results repeatedly proved that the limiting current  $i_L$  actually increases as the trend of bath temperature.

Excepting the bath temperature affecting the limiting current, the mechanical dynamics such as agitation and cupric ion concentration were two major mechanisms participating in the diffusion behavior of electrolyte. In Fig. 5, for the electrolyte with higher cupric ion concentration (90 g/l  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), the morphology of deposits was rougher than the electrolyte with lower cupric ion concentration (30 g/l  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) at a lower current density range. In Fig. 6, we found that resistivity for both cases initially decreased, the only difference between the two curves was that the resistivity of curve A (lower concentration) remained lower than curve B (higher concentration) before the biased current density was larger than 10 mA/cm<sup>2</sup>. After that bias value, the resistivity for a higher concentration was still on the downside but the resistivity of lower concentration began to increase. As shown in Fig. 7, when copper electroplating in the electrolyte with agitation, the morphology of copper film was rougher than that without agitation at lower current density region. Figure 8 showed the same trend as Fig. 6. The resis-

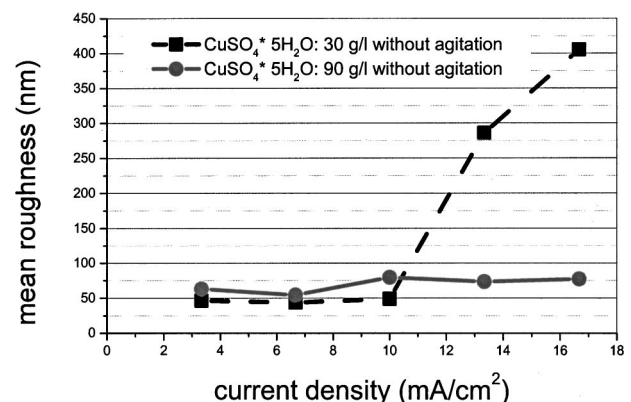


FIG. 5. Resistivity of copper deposits vs applied current densities and the cupric ion concentration relationship.

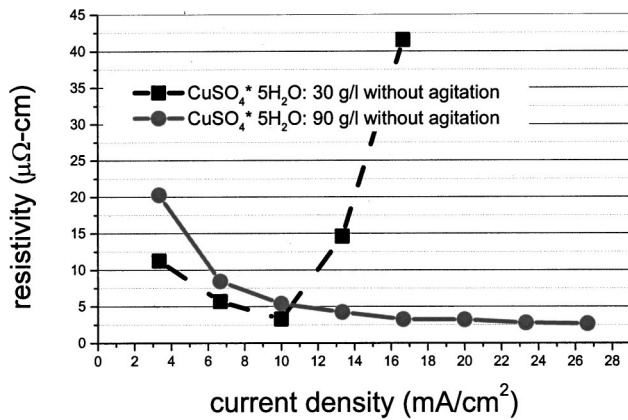


FIG. 6. Roughness of copper deposits vs applied current densities and the cupric ion concentration relationship.

tivity curve for the case with agitation monotonously decreased as the biased current density increased. Another curve without agitation changed as the trace for lower concentration in Fig. 6. In fact, the roles of the cupric ion concentration and agitation on morphology and resistivity of deposited films were, in principle, the same as the bath temperature. All of them typically shifted the limiting current to a larger value through modifying the diffusion dynamics of electrolytes and then the polarization effect decreased in the mass transport controlled dominated range. It becomes simple to understand that the resistivity or morphology for the case with smaller limiting current was always more perfect than another case with larger limiting current in the range of lower bias current.

Moreover, in Fig. 9, we could see a lower resistivity deposit obtained by using periodic pulse current plating as compared with direct current plating. Figure 10 displayed the AFM surface morphology at a constant density of  $1 \text{ mA/cm}^2$  for different plating wave forms. It showed the mean roughness ( $R_a$ ) in periodic pulse current plating (duty cycle: 50%, frequency: 1000 Hz) was 4.026 nm and in direct current plating was 6.195 nm. On the other hand, the mean roughness of sputtered copper was about 2.5–3.5 nm.

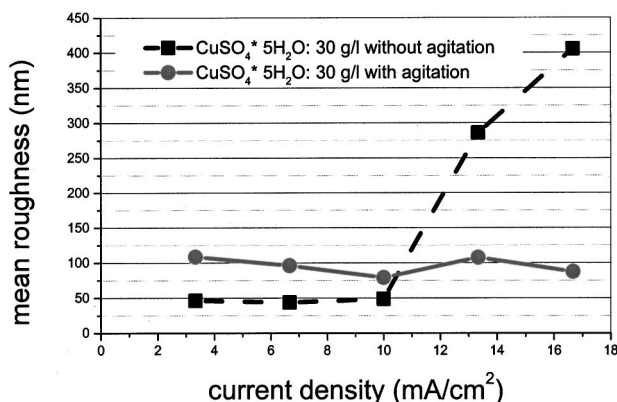


FIG. 7. Mean roughness ( $R_a$ ) of copper deposits vs applied current densities and agitation relationship.

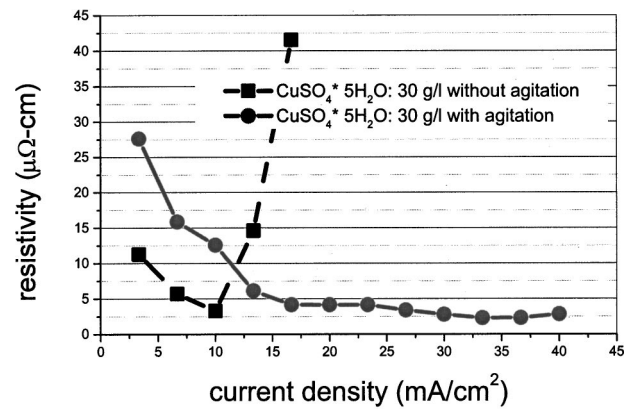


FIG. 8. Resistivity of copper deposits vs applied current densities and agitation relationship.

## B. Polarization effects on filling capability

In aspects of the gap-filling capability of electrodeposition in vias and trenches, we found that excellent filling capability was achieved at lower current density region. An excess of supplied current causes severe copper aggregation and nonuniform current distribution as shown in Fig. 11. The deposition rate is too high at the shoulder of vias/trenches to get complete filling. Based on the Butler–Volmer kinetics,<sup>8</sup> Takahashi and Gross defined a charge–transfer resistance and expressed as

$$R_{ct} = \frac{RT}{(\alpha_a + \alpha_c) i_0 A F} \quad (4)$$

for lower over potentials ( $|F\eta/RT| \ll 1$ ) where  $F$  is Faraday's constant,  $R$  is the gas constant,  $T$  is temperature,  $i_0$  is the average cathodic exchange current density,  $A$  is the electrode area,  $\alpha_a$  is the anodic transfer coefficient, and  $\alpha_c$  is cathodic transfer coefficient. For higher plating (negative) over potentials ( $|F\eta/RT| \gg 1$ ), the charge–transfer resistance was simplified as

$$R_{ct} = \frac{RT}{\alpha_c i_0 A F} \quad (5)$$

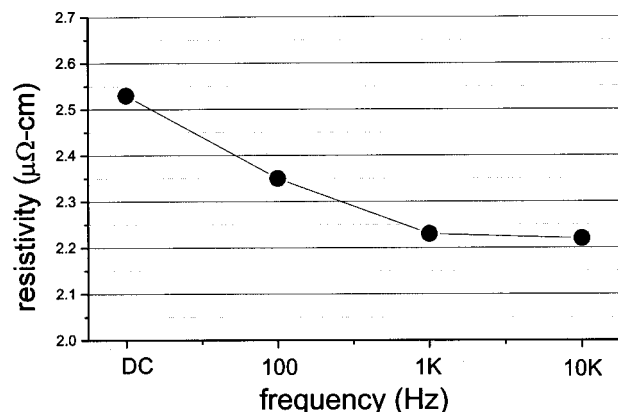


FIG. 9. Mean roughness ( $R_a$ ) of copper deposits vs different pulse frequencies at a constant density of  $3.33 \text{ mA/cm}^2$ .

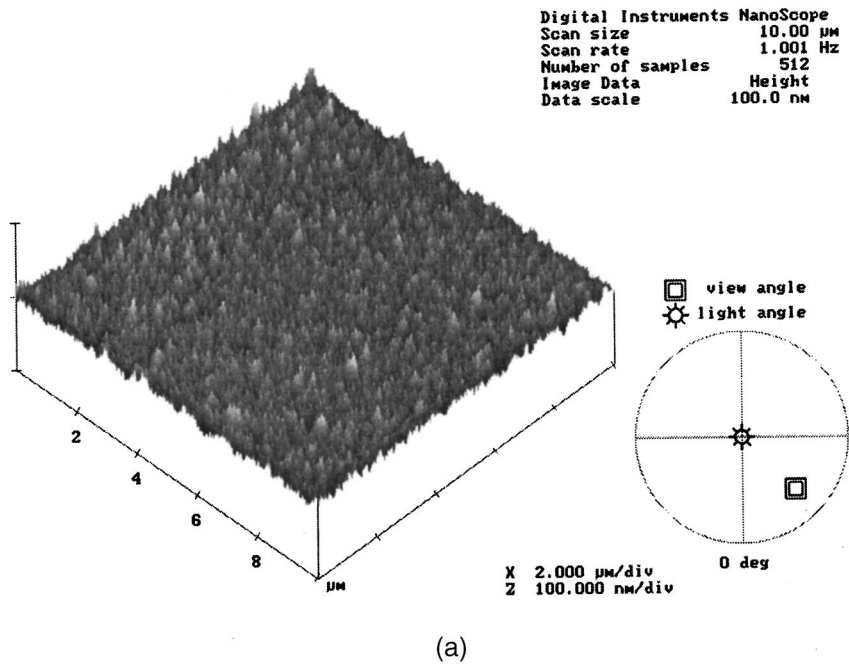
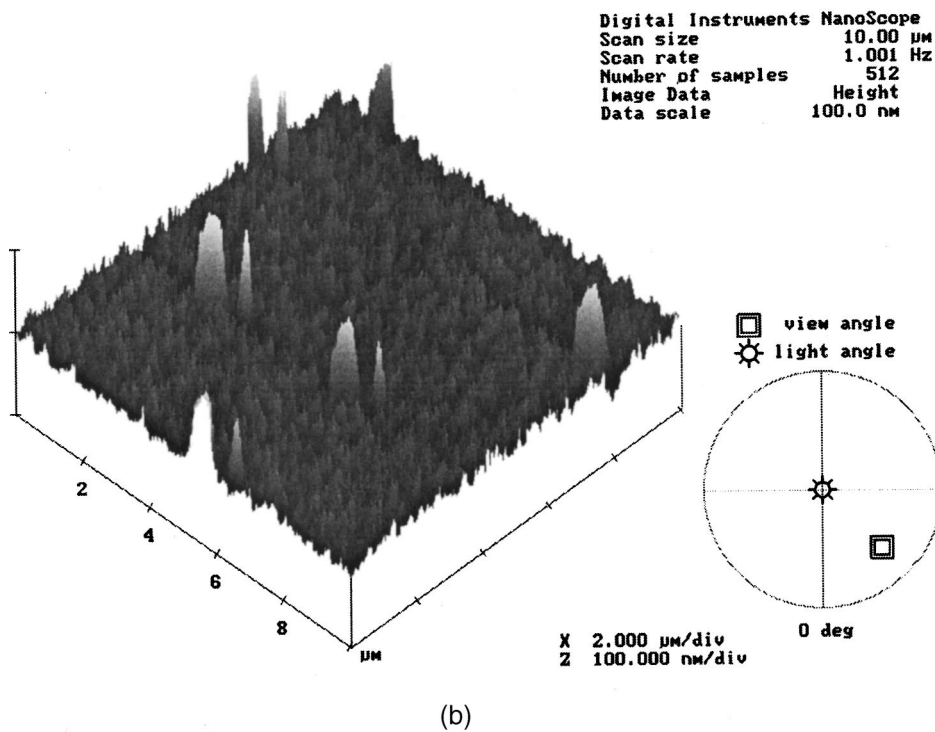


FIG. 10. AFM surface morphology at a constant density of  $1 \text{ mA/cm}^2$  for different plating wave forms: (a) the mean roughness ( $R_a$ ) in periodic pulse current plating (duty circle: 50%, frequency: 1000 Hz) and (b) in direct current plating.



In order to obtain higher quality films, we must control the electroplating process under higher over-potential range. According to Ohm's law, the current distribution in plating is affected by the polarization resistance of the double layer. When the polarization resistance increases, the current is more evenly distributed, which would result in higher throwing power.<sup>18</sup> Equation (5) indicates that the charge-transfer resistance is highest at low plating current density, leading to maximum plating uniformity and effective filling of vias/

trenches with minimum propensity for void formation. However,  $R_{ct}$  approaches a maximum at low current density ( $i_i/i_0 < 1$ ), defined by Eq. (4). Decreasing the magnitude of the dimensionless plating rate  $i_i/i_0$  or potential  $F\eta/RT$  below about 1 will not result in substantial improvements in plating uniformity. For this reason, the plating current must be controlled at an optimal value to improve filling capability and film quality simultaneously. On the other hand, we calculated the filling ratio  $\Delta y/\Delta x$  of "bottom up" to "side wall

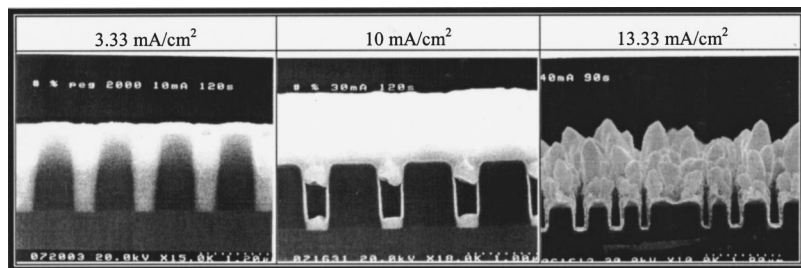


Fig. 11. Gap-filling profiles of SEM photos of copper electroplating with different applied current densities.

shift" from the cross section of a partially filled copper profile on the SEM photo to define the filling power of copper electroplating.<sup>9,10</sup> Figure 12 displayed the filling power ( $\Delta y/\Delta x$ ) of periodic pulse current plating for different current density, it also showed higher filling capability was operating at lower current density region.

Considering the effect of agitation on gap-filling capability, adding agitation can increase the limiting current density through reducing the diffusion layer  $\delta_N$  and enhancing the diffusion coefficient of cupric ions.<sup>17</sup> An increase of the diffusion coefficient of cupric ions and a decrease of the diffusion layer can improve the filling capability because more cupric ions can be furnished into the vias/trenches as seen in Fig. 13. But the influence of agitation on filling capability is limited, because the dimensions of vias/trenches in ULSI are small compared to the hydrodynamic boundary layer thickness and then diffusion behavior controls the mass transport in submicron trenches and vias.

For achieving the defect-free filling in submicron vias or trenches, the supplied current must be controlled at lower current density and the agitation must be acceded to the electroplating process. In previous study, Jiang and co-workers showed that it was advantageous to fill at room temperature (20 °C) due to better functionality in leveling of the additives. Additionally, the electrolyte must be composed of the proper amount of cupric ions,  $H_2SO_4$ , chloride ions, wetting agent, and filling promoter. In order to overstrike the threshold of an abruptly increasing gap-filling challenge in sub-0.2  $\mu m$  damascene feature, effective electrolyte obeying the adsorption–diffusion dynamics must simultaneously provide lower surface tension, sufficient inhibition on copper depositing and selective inhibition gradient within the feature.<sup>7</sup> Generally, adding a wetting agent can decrease interface en-

ergy between the electrolyte and the electrode surface and enhance cupric ions replenishing deep gaps. In addition to adding a wetting agent to reduce the surface tension, improving sufficient inhibition on copper depositing and selective inhibition gradient within the feature should be implemented by adding effective gap-filling promoter to plating baths. In our previous studies,<sup>9,10</sup> we demonstrated that the additive, 2-mercaptopyridine, could achieve defect-free filling, because it provided not only adequate overpotential but also selective inhibition gradient. However, the additives, 4-mercaptopyridine and thiourea, could not provide selective inhibition gradient, therefore, there were voids or seams with the damascene.

Additionally, in previous papers,<sup>18–21</sup> Kelly and co-workers showed that the leveling of 0.2  $\mu m$  trenches by an acid copper electrolyte with polyethylene glycol (PEG),  $Cl^-$ , bis(3-sulfopropyl) disulfide, and Janus Green B. Gau and co-workers demonstrated that copper could be electroplated into a 0.3  $\mu m$  dimension with an aspect ratio of 3 trenches by adding hydroxyl amine sulfate in the electrolyte.

In this study, the filling promoter consisted essentially of thiazole derivatives with benzyl-groups and amino-group ( $-NH_2$ ) such as 2-aminobenzothiazole. They offered sufficient inhibition on copper depositing and selective inhibition gradient. Moreover, PEG was employed in the electrolyte to reduce the surface tension within the small feature. Considering unitary effects of additives, there are three indispensable requirements for achieving super-filling property. They are a low surface tension of electrolyte, sufficient inhibition on copper depositing, and selective inhibition gradient. If those conditions are present simultaneously during electroplating, then super filling can be achieved. Also, we have optimized the appropriate amount of additives and achieve

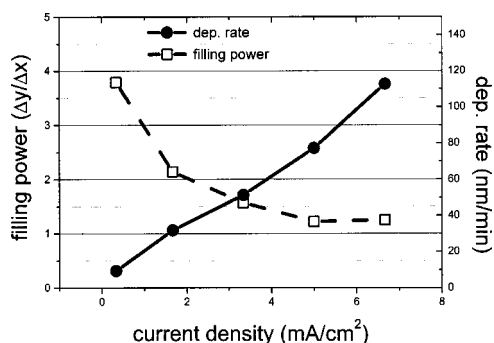


Fig. 12. Filling power ( $\Delta y/\Delta x$ ) vs different periodic pulse current density at constant frequency of 100 Hz.

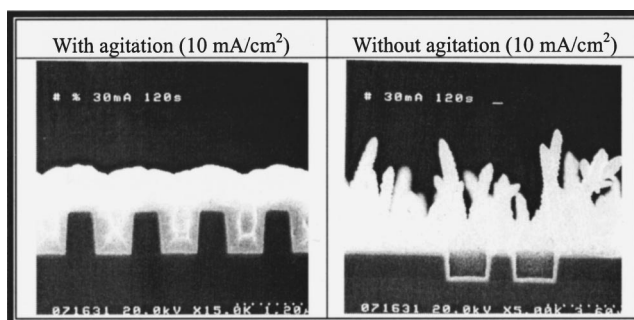


Fig. 13. Effects of agitation on gap-filling profiles of copper electroplating.

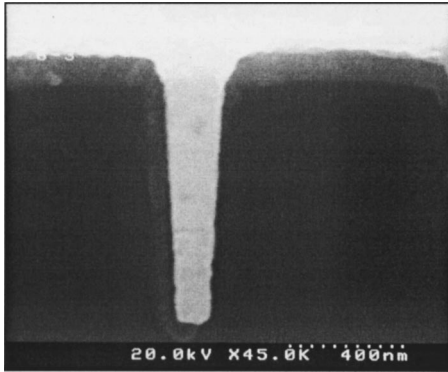


FIG. 14. The super filling is achieved in 130 nm with aspect ratio of 7 vias by using PEG as wetting agent and 2-aminobenzothiazole as filling promoter in periodic pulse current plating (duty circle: 50%, frequency: 100 Hz, and current density: 1 mA/cm<sup>2</sup>).

the super-filling performance for 0.13  $\mu\text{m}$  vias with aspect ratio of 7 by an acid-copper electrolyte as shown in Fig. 14.

#### IV. CONCLUSIONS

Lower resistivity and uniformly distributed copper film can usually be obtained from the process electrolytes that are capable of being operated at a larger over potential. In order to enhance the filling capability in submicron vias or trenches, the supplied current must be controlled at lower current density and the agitation must be acceded to the electroplating process. Low surface tension of electrolyte, sufficient inhibition on copper depositing, and selective inhibition gradient are three indispensable conditions for achieving super-filling property. Thiazole derivatives with benzyl-

groups and amino-group ( $-\text{NH}_2$ ) could offer sufficient inhibition on copper depositing and selective inhibition gradient, and then the defect-free filling was achieved in 0.13  $\mu\text{m}$  vias with aspect ratio of 7. Moreover, a lower resistivity film and higher filling capability could be obtained by using periodic pulse current plating as compared with direct current plating.

#### ACKNOWLEDGMENTS

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