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Copper electroplating for future ultralarge scale integration interconnection

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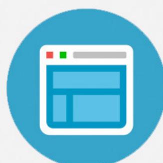
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Copper electroplating for future ultralarge scale integration interconnection*

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Copper has received considerable attention during the past few years because of its low electrical resistivity, high melting temperature, and high electromigration resistance. Since electrochemical plating has several advantages compared to physical vapor deposition and chemical vapor deposition due to its low cost and low processing temperature, it becomes the most attractive technique for the implementation of Cu metallization. In this article, we report an electroplating scheme for Cu deposition and study aspects of copper electroplating related to chemical additives effected on Cu deposition. A low resistivity Cu film ($\sim 2\ \mu\Omega\,\mathrm{cm}$) could be obtained when metallic ion concentration is decreased or current density is increased. The detailed correlation between film resistivity, electrolyte concentration, current density, and film morphology is given in this study. In addition, chemical additives in electrolyte solutions also play important roles in copper electroplating. In this report, thiourea and polyethylene glycol, which are usually added in printing circuit board electroplating to influence nucleation, have been used as gap filling promoters to help Cu filling. The results show that addition of thiourea and polyethylene glycol could help in forming smooth Cu film but does not promote Cu filling ability. Hydroxyl amine sulfate, which has both amino and sulfate groups, is proposed for use as a gap filling promoter in helping Cu electroplating. In this work, we demonstrate that Cu could be electroplated into fine trenches (at 0.3 μm dimension with aspect ratio of 3) when hydroxyl amine sulfate is present and no voids are formed. © *2000 American Vacuum Society.* [S0734-2101(00)07602-8]

I. INTRODUCTION

As device scales are narrowed down to deep submicron dimensions, the signal propagation is dominated by interconnection performance, but not by transistor switching speed.[1] The performance of interconnection is dependent on its resistance and capacitance. In order to increase signal propagation speed, low resistivity metallization materials play very important roles in the ultralarge scale integration (ULSI) metallization.[2,3]

Recently, copper has attracted considerable attention as a potential ULSI metallization material, because of its low electrical resistivity and high electromigration resistance compared with aluminum.[4] Copper could be deposited by most conventional methods such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). However, a simple method of electrochemical plating could be used to deposit Cu film as well. Electrochemical plating has several advantages compared to PVD and CVD due to its low cost, low processing temperature, and good ability to fill vias.[4] Therefore, electroplating is becoming the leading technique in copper metallization for future ULSI interconnection.[5,6]

A conventional solution for Cu electroplating contains several electrolytes and additives. The roles which these electrolytes and additives play are to control plating process and obtain good deposition quality. A fundamental understanding of these substances roles is still deficient.

In this report, we study the relationships between film resistivity, electrolyte concentrations, and current density. Second, we alter some operation conditions to study the correlation of film resistivity with film morphology. Finally, the effect of conventional additives, e.g., thiourea[7] and polyethylene glycol[8] on Cu electroplating is described as well. A

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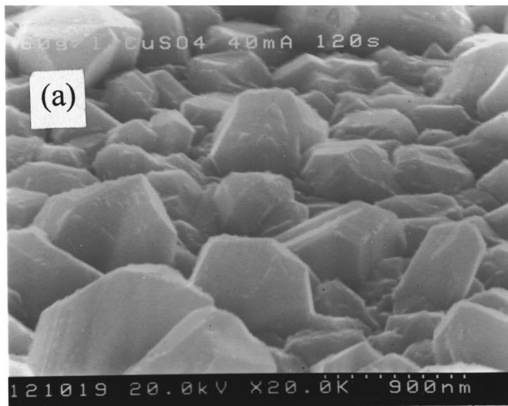
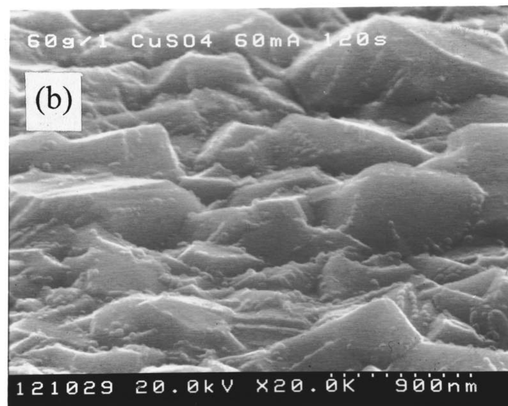




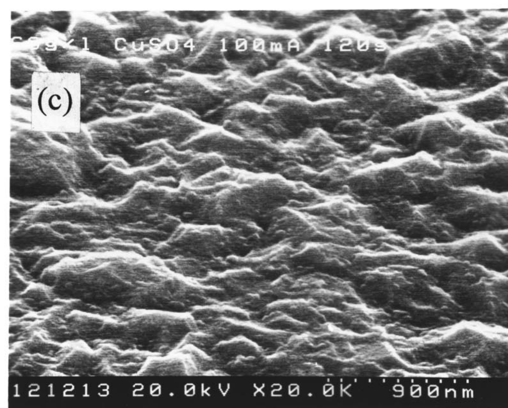
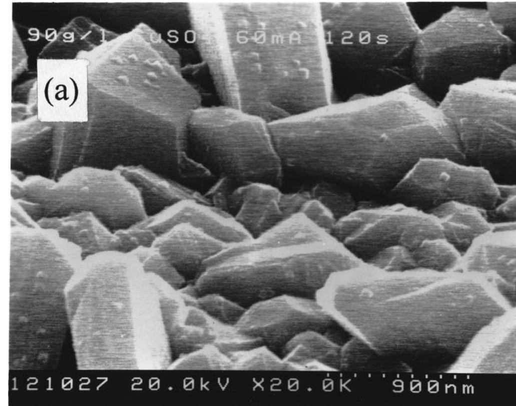


FIG. 1. Dependence of film morphology on current density when cupric sulfate kept at 60 g/ℓ and deposition time at 120 s. Current density is (a) 1.6, (b) 2.4, and (c) 4.0 A/dm^2.

novel additive of $(NH_2OH)_2 \cdot H_2SO_4$, which could be used as a gap filling promoter, helping Cu electroplating is demonstrated in this work.

II. EXPERIMENT

Cu electroplating is performed on a *p*-type silicon substrate with (100) orientation. The substrate is deposited with a 150-nm-thick Cu seed layer and 40 nm of ionized metal sputtered TaN. The TaN is used as a diffusion barrier, which is located at the bottom of Cu seed layer. The Cu electroplating is directly deposited on the seed layer. The seed layer



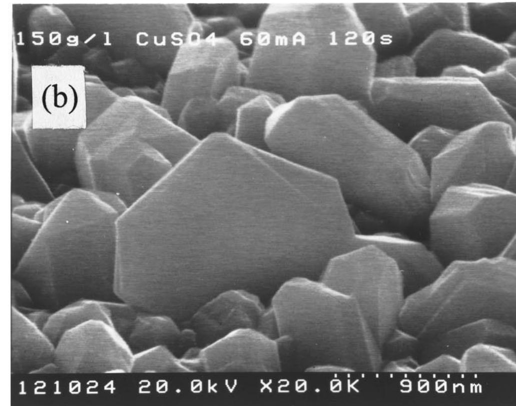


FIG. 2. Dependence of film morphology on copper ion concentration when current density kept 2.4 A/dm^2 and deposition time at 120 s. Concentration of cupric sulfate of 90 and 150 g/ℓ is shown in (a) and (b), respectively. Concentration of cupric sulfate of 60 g/ℓ is shown in Fig. 1(b).

provides a conduction line of low resistance for electroplating current, which drives deposition occurring and facilitates film nucleation as well. A traditional Cu electroplating solution usually contains 60–150 g/ℓ of $CuSO_4 \cdot 5H_2O$, 80–150 mI/l of H_2SO_4 50–150 ppm of HCl and some chemical additives. The copper (II) sulfate solution dissociates in the highly acidified solution to produce Cu^{2+} and SO_4^{2-}ions. The silicon substrate (cathode) is connected to a negative potential, at which Cu^{2+} reduction occurs. The copper electrode (99.95% Cu, 0.05% P) (anode) is connected to a positive potential, copper metal is oxidized to produce Cu^{2+}ions and dissolved in the solution.

The film properties are studied by altering concentrations of electroplating solution and current density (1–4 A/dm^2). The deposited copper film is characterized by using scanning electron microscopy for morphology inspection and thickness measurement. The crystal structure is examined by using x-ray diffraction. In addition, the effects of chemical additives of thiourea, polyethylene glycol, and hydroxyl amine sulfate on Cu electroplating are described.

III. RESULTS AND DISCUSSION

The film resistivity and film morphology are largely dependent on electrolyte concentration and current density. Figures 1–3 present our experimental results, which indicate

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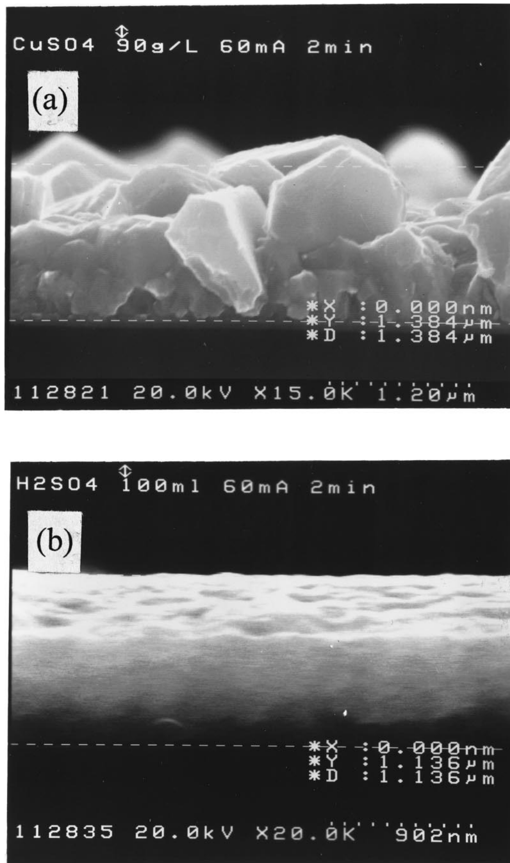


FIG. 3. Dependence of film morphology on concentration of sulfuric acid when current density kept at 2.4 A/dm^2, $CuSO_45H_2O$ at 90 g/ℓ, and deposition time at 120 s. Concentration of sulfuric acid is (a) 0 and (b) 70 g/ℓ.

the correlation of film morphology with electrolyte concentration and current density without the addition of chemical additives. As shown in Figs. 1–3, a smooth surface of Cu film could be obtained when either increasing current density, increasing concentration of sulfuric acid, or decreasing concentration of cupric sulfate. The smoother surface of Cu film makes its resistivity lower. The relationship between film morphology and film resistivity is shown in Figs. 4 and 5. Detailed reaction mechanisms of Cu electroplating could

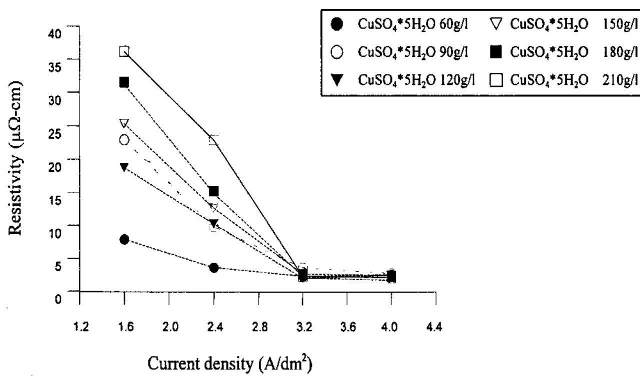


FIG. 4. Dependence of film resistivity on various cupric ion concentration (60–210 g/ℓ) at different current density when deposition time is kept at 120 s.

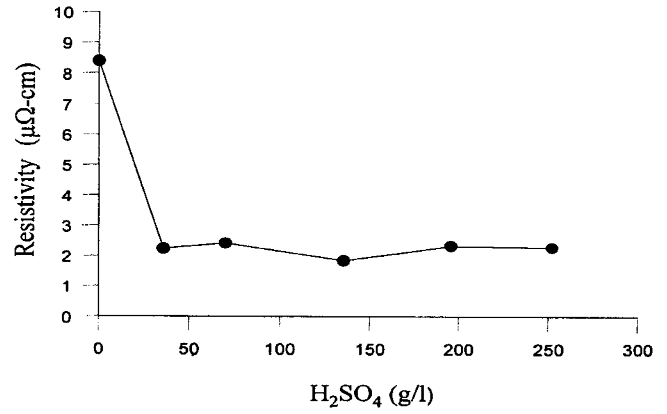
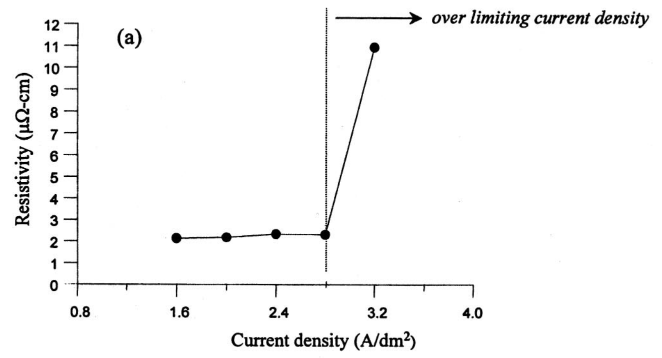


FIG. 5. Dependence of film resistivity on concentration of sulfuric acid. The concentration of cupric sulfate is kept at 90 g/ℓ and current density is 2.4 A/dm^2.



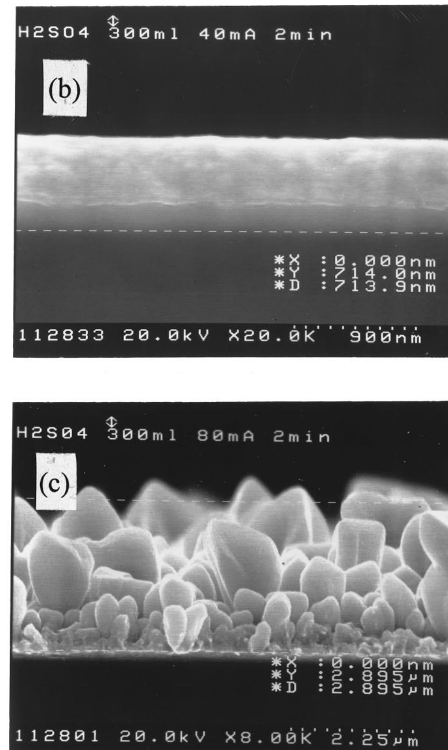


FIG. 6. (a) Correlation of film resistivity with current density when $CuSO_4$ at 90, H_2SO_4 at 197 g/ℓ, and deposition time at 120 s. The effect of current density on film morphology when current density is (b) at 1.6 and (c) at 3.2 A/dm^2.

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be interpreted as follows. Two reaction schemes govern the Cu electroplating: one is the electrode surface reaction; another is Cu^{2+} diffusion from the electrolyte solution to the electrode surface. Polarization occurs when the rate of Cu^{2+} supply from the electrolyte solution is not faster than the rate of reaction at the electrode surface. The film morphology is governed by the degree of polarization.[9] The higher polarization would make electroplating slower to produce a smoother film. Since the effect of increasing current density is to increase the electrode surface reaction, a faster surface reaction makes Cu^{2+} undersupplied from the electrolyte solution; therefore, the polarization is higher and smoother film morphology is observed. In addition, decreasing the $CuSO_4$ concentration and increasing the H_2SO_4 concentration will make Cu^{2+} diffusion even slower and increase polarization. Thus, a smooth surface with small grain Cu film is observed.

However, increasing the H_2SO_4 concentration produces a smooth Cu film surface, but decrease the limiting current density [Figs. 6(a) and 6(b)]. When the applied current density is greater than a limiting current density, it is impossible for the electrode to gain any Cu ions from the electrolyte solution; therefore, the large Cu grains could result from redissolution and redeposition [Fig. 6(c)]. In addition, the orientation of Cu film is measured by x-ray diffraction and results are shown in Fig. 7. The (111) orientation is preferred because it has higher electromigration resistance. As shown in Fig. 7, crystal orientation is not sensitive to current density when current density is not over the limiting current density. A high ratio of (111)–(002) orientation is observed when current density is over the limiting current density. Therefore, in order to obtain adequate deposition rate with low resistivity and smooth Cu⟨111⟩ film, adding the proper amount of sulfuric acid and keeping proper current density are necessary.

Various additives are added in solution to help Cu electroplating in order to get good deposition profile. In this study, we attempted to use thiourea and polyethylene glycol as gap filling promoters, because both chemicals have a lone pair of electrons which could inhibit Cu ion aggregation in the peak region of feature dimension. The results are shown in Fig. 8. Voids are still formed when thiourea and polyethylene glycol are added.

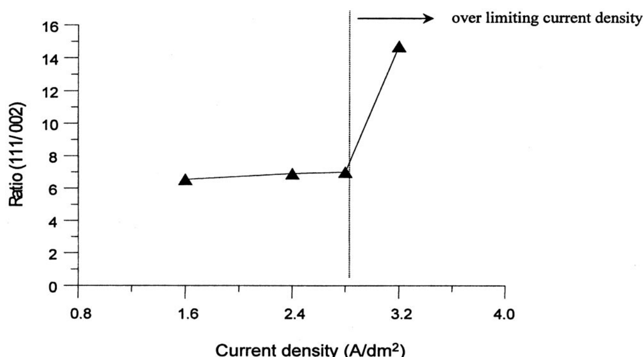

FIG. 7. Dependence of crystal orientation on current density when $CuSO_4$ at 90 H_2SO_4 at 197 g/ℓ, and deposition time at 120 s.

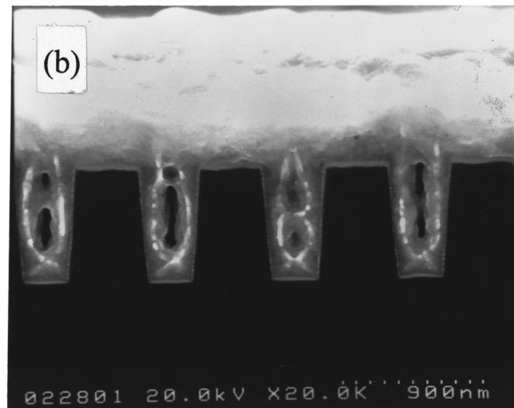

FIG. 8. Cu electroplating in 0.3 □m trenches (a) with thiourea (0.02 g/ℓ) addition, and (b) with polyethylene glycol (0.1 g/ℓ) addition. The concentrations of cupric sulfate and sulfuric acid are 90 and 197 g/ℓ, respectively. The applied current density is 1.2 A/dm^2.

A novel chemical additive of hydroxyl amine sulfate $[(NH_2OH)_2 \cdot H_2SO_4]$, which has both amino and sulfate groups, is prepared for use as a gap filling promoter because it dissolves into small molecules with a lone pair of electrons around the nitrogen atom. 0.3 μm wide of fine trenches with an aspect ratio of 3 have been electroplated. No voids are observed when hydroxyl amine sulfate is present (see Fig. 9).

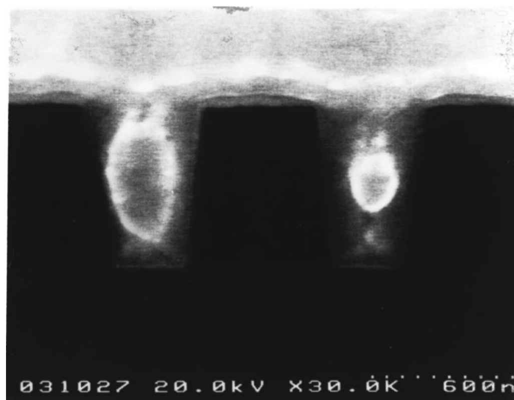

FIG. 9. Cu electroplating in 0.3 □m trenches with hydroxyl amine sulfate addition (0.06 g/ℓ). The concentrations of cupric sulfate and sulfuric acid are 90 and 197 g/ℓ, respectively. The applied current density is 1.2 A/dm^2.

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The filling mechanism is unknown. A further study of the filling mechanism is needed.

IV. CONCLUSIONS

The mechanisms of Cu electroplating are given in this study. The film morphology and film resistivity are dependent on electrolyte concentrations and applied current density. These relationships could be described using polarization theory. In order to get a good deposition profile with lower Cu film resistivity, adding a suitable chemical additive into the electrolyte solution could help Cu electroplating. In this work, we demonstrate that a novel chemical additive of hydroxyl amine sulfate could be used as a gap filling promoter in helping Cu electroplating without void formation.

ACKNOWLEDGMENTS

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[1]A. R. Sethuraman, J.-F. Wang, and L. M. Cook, J. Electron. Mater. **25**, 1617 (1996).
[2]D. C. Edelstein, Proc. Of VMIC, June, 1995, p. 301.
[3]P. Singer, Semicond. Int. 91 (1998).
[4]S. P. Muraka and S. W. Hymes, Crit. Rev. Solid State Mater. Sci. **20**, 87 (1995).
[5]V. M. Dubin, C. H. Ting, and R. Cheung, Proc. Of 14th VMIC Conference, 1997, p. 69.
[6]P. Andricacos, Interface 32 (1999).
[7]D. Papapanayiotou, R. N. Nuzzo, and R. C. Alkire, J. Electrochem. Soc. **145**, 3366 (1998).
[8]J. J. Kelly and A. C. West, J. Electrochem. Soc. **145**, 3472 (1998).
[9]F. Lowenheim, *Modern Electroplating*, 3rd ed. (Wiley, New York, 1989), Chap. 1.

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