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Improving the quality of electroplated copper films by rapid thermal annealing

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The leveler, 2-mercaptopyridine (2MP), increases the filling power of copper electroplating electrolytes in plating 0.15 μm vias, but forms the plated copper metals of small-grained column structures with high resistivity. In this study, we used rapid thermal annealing (RTA) to effectively improve the film quality. After RTA at 400 °C for 30 s, the resistivity of Cu deposits was reduced from ~ 16.1 to ~ 2.4 $\mu\Omega\text{cm}$. Moreover, the Cu(111) intensity of Cu deposits increased after RTA annealing. © 2003 American Vacuum Society. [DOI: 10.1116/1.1562641]

I. INTRODUCTION

Cu electroplating has become a promising technology for producing copper interconnects in a damascene structure. In particular, a plating bath should introduce a diffusion-limited leveler to result in a higher copper deposition rate at the bottom of the features than at the sidewalls, to yield excellent filling. In agreement with previous reports of the chemistries used to achieve superfilling in sub-0.2 μm Cu electroplating, description of the combined effects of chloride ion (Cl^-), polyethylene glycol (PEG), and other filling promoters have recently been published by many groups.^{1–4} Although additives with depletion (adsorption) reactions can be used to enhance the gap-filling efficiency, the incorporation of impurities may lead to electroplated Cu films having a much higher electrical resistivity than the bulk value.⁵ According to the mathematical model developed by West and co-workers,⁶ a dimensionless R_{LA} ($\sim k/D$) was proposed as the design rule for the void-free deposition; where D and k are the diffusion coefficient and the consumption rate constant of an additive, respectively. An effective additive must not only have an appropriate value of R_{LA} to generate a concentration gradient within a feature but also produce a low-resistivity Cu film. In our previous study, superfilling phenomenon was achieved in 0.15 μm vias using 2-mercaptopyridine (2MP) as the leveling agent, because 2MP provided not only adequate overpotential but also selective inhibition gradient.³ However, 2MP produced a high-resistivity film due to its high consumption rate into deposited films and its small-grained column structure.⁷

In this work, we used rapid thermal annealing (RTA) to reduce the resistivity of Cu films and to prevent time-consuming and high-temperature furnace annealing, which is harmful for low- k material integrated processes. RTA is con-

ventionally used for process steps such as dopant activation,⁸ dopant redistribution,⁹ formation of metal silicides,¹⁰ and improving the barrier capability in a Cu metallization system.¹¹ In this study, the resistivity of as-deposited Cu films was about 16.1 $\mu\Omega\text{cm}$ using the electrolyte with 2MP as the filling promoter. After RTA at 400 °C for 30 s, the resistivity was dramatically reduced to ~ 2.4 $\mu\Omega\text{cm}$. Additionally, the changes of grain size and electrical resistivity were monitored to determine the effect of electrolyte compositions in electroplated Cu films at room temperature and elevated temperatures.

II. EXPERIMENT

The blanket wafer used in this study was prepared by sputter depositing a 50-nm-thick TaN diffusion barrier and a 50-nm-thick Cu conduction layer on SiO_2 . The patterned wafer was composed of a 30-nm-thick ionized metal plasma (IMP)–TaN layer as the diffusion barrier and a 200-nm-thick IMP–Cu film as the seed layer. In the Cu electroplating processes, the standard electrolyte was composed of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (30 g/l), H_2SO_4 (275 g/l), and chloride ions (50–100 ppm). The films were deposited under galvanostatic control at room temperature. All the Cu electroplating for films was performed under a constant current density of 0.001 A/cm^2 except when films were deposited using the standard electrolyte due to a weaker polarization effect in the latter electrolyte (without additives) that necessitated a higher bias current for maintenance of minimal resistivity in deposited films in which case 0.01 A/cm^2 was used. The cross-sectional profiles of Cu films were examined using a field emission scanning electron microscope (FESEM) and surface morphologies were measured using an atomic force microscope (AFM) from DI Nanoscope. Potentiodynamic (PD) polarization measurement performed on an EG&G potentiostat/galvanostat (model 273A) was used to analyze the electrochemical behaviors of electrolytes. The counterelectrode was

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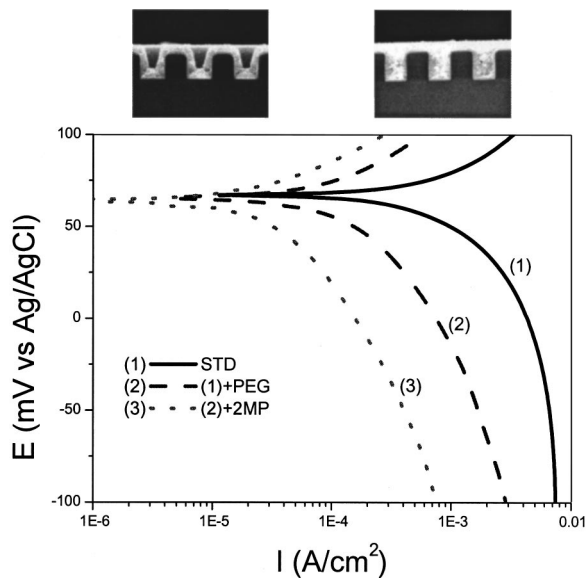


FIG. 1. SEM cross-sectional profiles: superfilling transient mechanism in 1 μm vias using the electrolyte containing 2MP; steady-state i - E characteristics for copper deposition from various electrolytes.

platinum and the working electrode was Cu with a constant surface area of 0.5 cm^2 . All potentials are reported relative to the Ag/AgCl electrode, which was used as the reference electrode. An x-ray diffractometer (XRD) was utilized to investigate crystal orientation of the electroplated Cu films and differential scanning calorimetry (DSC) was performed on the electroplated Cu films to characterize the microstructure. The chemical composition was determined using x-ray photoelectron spectroscopy (XPS). The XPS analyses were performed using a VG ESCA 210 instrument, with excitation by Mg $K\alpha$ radiation ($h\nu=1253.6$ eV). After electroplating, the specimens were annealed from 200 to 550 $^{\circ}\text{C}$ for 30 s in N_2 atmosphere and the sheet resistances of Cu deposits were measured by a four-point probe.

III. RESULTS AND DISCUSSION

In our previous work, we found that in the electrolyte containing PEG and 2MP, a complete filling was obtained in 0.15 μm vias because 2MP enabled a selective inhibition gradient.³ The adsorption–diffusion model combined with cathode polarization and cyclic voltammetric stripping measurements were also employed to explain the attribution of additives in superfilling phenomena.³ Scanning electron microscopy (SEM) cross-sectional profiles in Fig. 1 show the superfilling transient mechanism in 1 μm vias using the electrolyte containing 2MP. Although 2MP provided a high lev-

eling power, a high-resistivity film (>8 $\mu\Omega\text{cm}$) was obtained after deposition.⁷ Tafel plots in Fig. 1 reveal that 2MP raised the charge transfer resistance and inhibited Cu deposition. At a constant current density of 0.001 A/cm^2 , the shifted overpotential, caused by the added PEG, was 61.7 mV relative to that of the standard solution (STD) and the related value for the combined action of PEG–2MP was 200.1 mV. Table I summarizes the XPS data of the Cu films electroplated in STD with PEG and 2MP. The presence of nitrogen (N) atoms in the Cu films indicates that 2MP was chemisorbed on or consumed by the deposit. According to Cunningham's investigation,¹² we propose one factor to describe the influences of characteristic impurities on the resistivity of deposits. This impacting factor f is expressed as $f=4*C+5.5*O+7*N+9*S$ (C, O, N, and S denote the atomic percentages of C, O, N, and S atoms in the deposits, respectively) and the calculated f of various electrolyte chemistries are in the following order: STD+PEG+2MP (5.33) $>$ STD+PEG (3.35) $>$ STD (3.01). The electrical resistance of blanket films is usually used to probe the influence of additive chemistries on impurity incorporation and its effect on microstructural evolution. The initial resistivities of as-deposited films (average thickness of about 300 nm) deposited using different electrolytes are as follows: STD+PEG+2MP (16.1 $\mu\Omega\text{cm}$) $>$ STD+PEG (2.2 $\mu\Omega\text{cm}$) $>$ STD (2.1 $\mu\Omega\text{cm}$). The added 2MP apparently increased the resistivity of deposited films due to its higher impurity incorporation and small-grained columnar structure.⁷ Figure 2(a) shows that the electrolyte with 2MP formed a columnar structure; this type of grains was the result of a preferred growth in certain crystal directions. The field orientated texture type (FT) is usually observed at fairly strong inhibition and is characterized by a large number of elongated crystals perpendicular to the substrate, forming a coherent deposit.¹³ Besides, it was found that random-orientated grains were formed by the STD and STD+PEG electrolytes [Fig. 2(b)] and they had relative larger sizes than the case of a columnar structure. Comparisons between grain growth types predicted that the STD+PEG+2MP electrolyte would generate a higher electrical resistivity than other electrolytes.⁷

Electroplated Cu films are typically deposited at room temperature by a galvanostatic or a potentiostatic process, and are metastable immediately after deposition. The as-deposited films transform into larger-grained structures at room temperature by self-annealing. However, the driving force for grain growth derived from reduction in grain boundary energy and reduction of microstrains and/or defects is limited. To further reduce the grain boundary surface area, the input of additional energy is required.¹⁴ The goal of

TABLE I. XPS data for the copper films electroplated in various electrolytes; C, O, N, and S denote the atomic percentage of C, O, N, S atoms in the deposits.

	Cu	C	O	N	S	$F=4*C+5.5*O+7*N+9*S$
STD	36.63%	40.39%	19.37%	0%	3.61%	3.01
STD+PEG	35.59%	24.91%	34.44%	0%	5.06%	3.35
STD+PEG+2MP	11.57%	14.02%	33.46%	34.26%	5.89%	5.33

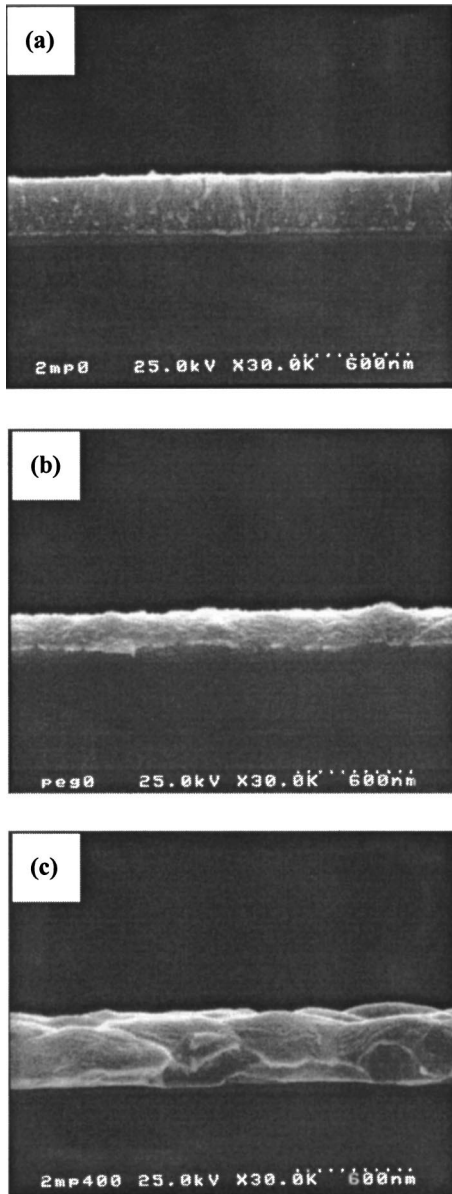


FIG. 2. SEM cross-sectional profiles of Cu films.

this study is to introduce RTA to improve film quality. We found that an increase of annealing temperature (300–550 °C) enhanced grain growth and the obvious grain growth started at 400 °C, as seen in Fig. 3. On the other hand, the

	as-deposited	300°C	400°C	450°C	550°C
Standard solution					
Std. + PEG					
Std. + PEG + 2MP					

FIG. 3. Plane views of AFM images (5 μm×5 μm) of annealed (300–550 °C) and as-deposited films.

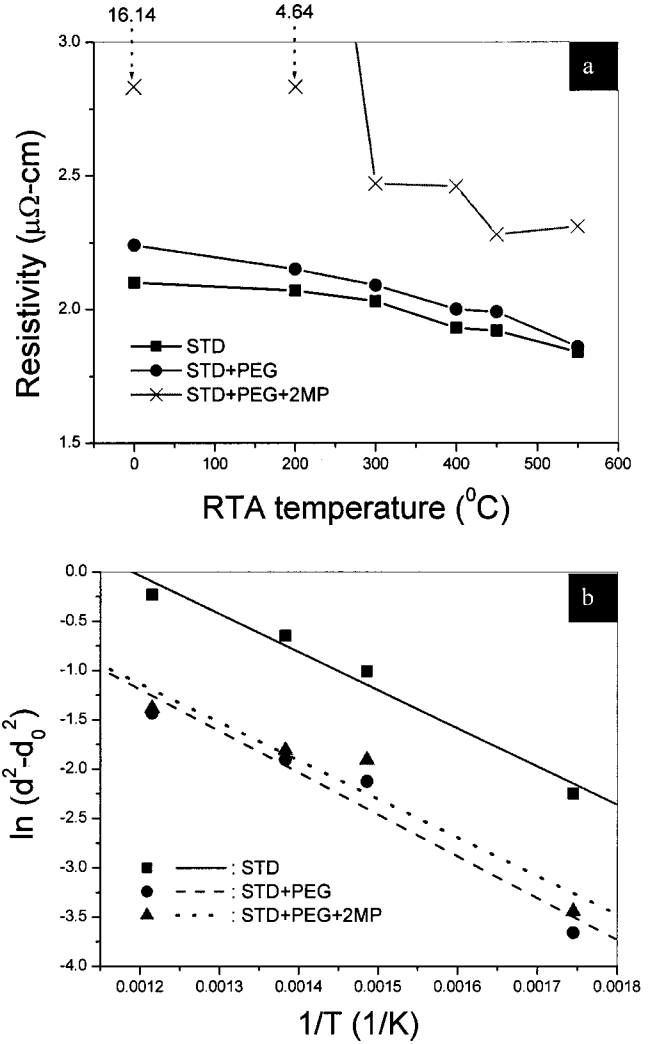


FIG. 4. (a) Effect of electrolyte chemistries on resistivity transients of deposited films by RTA from 200 to 550 °C. All of the additives had the same concentration of 50 ppm; (b) Arrhenius plots of $\ln(d^2-d_0^2)$ vs the reciprocal of absolute temperature from 300 to 550 °C.

film resistivity decreased with annealing temperature as shown in Fig. 4(a). After RTA at 400 °C for 30 s, the resistivity of Cu films deposited using the STD+PEG+2MP electrolyte was obviously reduced to $\sim 2.4 \mu\Omega \text{ cm}$. The SEM cross-sectional profile in Fig. 2(c) shows that the small-grained column structure [see Fig. 2(a)] disappeared after RTA at 400 °C for 30 s. For the Arrhenius model, the mean diameter for the thermal-induced grain boundary migration could be expressed with the annealing time t according to the relationship¹⁴

$$R = \frac{d^n - d_0^n}{t} = R_0 \exp(-Q/kT), \tag{1}$$

where Q is the thermal activation energy for grain growth, d and d_0 are the mean grain size of the annealed and the as-deposited films, respectively, and R and n are time-independent constants; the exponent n is set at its usual value of 2. Figure 4(b) shows the Arrhenius plot of $\ln(d^2-d_0^2)$ versus the reciprocal of the absolute temperature from 300 to

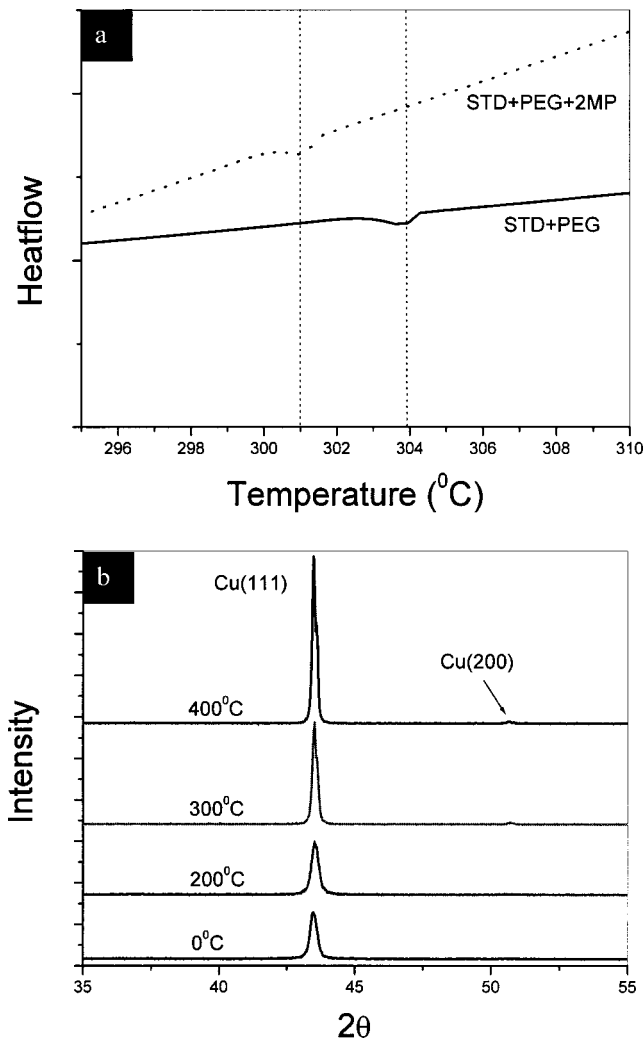


Fig. 5. (a) Differential scanning calorimetry thermogram of as-deposited Cu films; (b) Cu(111) intensity transients with RTA temperature for the STD+PEG+2MP electrolyte.

550 °C. The slope of the plot gives the activation energy for the grain growth of the electroplated Cu film. The activation energies of grain growth were 0.33, 0.36, and 0.34 eV for the electrolytes STD, STD+PEG, and STD+PEG+2MP, respectively. Notably, the activation energy for grain growth of the STD+PEG+2MP electrolyte was lower than that of the STD+PEG electrolyte. This may be due to that the preferred orientation structure (column structure), deposited using the electrolyte with 2MP, had lower interface energies between grains. Using DSC, the energy change associated with the material transformation process was examined and is shown in Fig. 5(a). Exothermic peaks were found on as-deposited specimens. These peaks were attributed to the grain growth of electroplated Cu films. The peak of the film deposited using the STD+PEG+2MP electrolyte appeared at lower

temperature (~ 301 °C) than that of the film deposited using the STD+PEG (~ 304 °C) electrolyte. This result also confirmed that the added 2MP could lower the activation energy of Cu grain growth, as shown in Fig. 4(b).

In addition to grain size, another important factor for electrical performance is the crystallographic texture of the Cu. The crystallographic texture of Cu is face-centered-cubic (fcc) and (111) is the closed packed plane in fcc structures. Therefore, (111) has higher electromigration resistance than other planes of the fcc structure.¹⁵ Figure 5(b) shows the x-ray diffraction patterns obtained for the as-deposited and annealed films deposited using the STD+PEG+2MP electrolyte. It was found that the films mainly consisted of (111) preferred orientation and the Cu(111) intensity increased with RTA annealing temperature.

IV. CONCLUSIONS

The resistivity of the Cu films deposited using the electrolyte with 2MP as the leveler was effectively reduced from $\sim 16.1 \mu\Omega \text{ cm}$ to $\sim 2.4 \mu\Omega \text{ cm}$ after RTA at 400 °C for 30 s. The high-resistivity film deposited using the electrolyte with 2MP had lower activation energy (0.34 eV) for grain growth than that (0.36 eV) of the film deposited using the electrolyte without 2MP during RTA annealing (300–550 °C). This result occurred due to lower interface energies between grains of the preferred orientation structure (column structure).

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- ¹J. J. Kelly, C. Tian, and A. C. West, *J. Electrochem. Soc.* **146**, 2540 (1999).
- ²T. P. Moffat, J. E. Bonevich, W. H. Huber, A. Stanishevsky, D. R. Kelly, G. R. Stafford, and D. Josell, *J. Electrochem. Soc.* **147**, 4524 (2000).
- ³S. Y. Chiu, J. M. Shieh, S. C. Chang, K. C. Lin, B. T. Dai, C. F. Chen, and M. S. Feng, *J. Vac. Sci. Technol. B* **18**, 2835 (2000).
- ⁴S. C. Chang, J. M. Shieh, K. C. Lin, B. T. Dai, C. F. Chen, T. C. Wang, M. S. Feng, Y. H. Li, and C. P. Lu, *J. Vac. Sci. Technol. B* **19**, 767 (2001).
- ⁵C. Alonso, M. J. Pascual, and H. D. Abruna, *Electrochim. Acta* **42**, 1739 (1997).
- ⁶A. C. West, *J. Electrochem. Soc.* **147**, 227 (2000).
- ⁷C. F. Chen and K. C. Lin, *Jpn. J. Appl. Phys., Part 1* **41**, 1981 (2002).
- ⁸Y. T. Kim, H. J. Yoo, C. H. Jun, W. I. Jang, and S. H. Kim, *J. Vac. Sci. Technol. A* **7**, 796 (1989).
- ⁹T. Inada, S. Wakabayashi, and H. Iwasaki, *J. Appl. Phys.* **69**, 6665 (1991).
- ¹⁰K. Shenai, P. A. Piacente, N. Lewis, G. A. Smith, M. D. McConnell, and B. J. Baliga, *J. Vac. Sci. Technol. B* **6**, 1728 (1988).
- ¹¹S. K. Rha, S. Y. Lee, W. J. Lee, Y. S. Hwang, and C. O. Park, *J. Vac. Sci. Technol. B* **16**, 2019 (1998).
- ¹²J. A. Cunningham, *Semicond. Int.* **23**, 95 (2000).
- ¹³R. Winand, *Electrochim. Acta* **39**, 1091 (1994).
- ¹⁴C. H. Seah, S. Mridha, and L. H. Chan, *J. Vac. Sci. Technol. A* **17**, 1963 (1999).
- ¹⁵C. Lingk, M. E. Gross, and W. L. Brown, *Appl. Phys. Lett.* **74**, 682 (1999).