

Effect of plating current density and annealing on impurities in electroplated Cu film

Chi-Wen Liu, Ying-Lang Wang, Ming-Shih Tsai, Hsien-Ping Feng, Shih-Chieh Chang, and Gwo-Jen Hwang

Citation: *Journal of Vacuum Science & Technology A* **23**, 658 (2005); doi: 10.1116/1.1931679

View online: <http://dx.doi.org/10.1116/1.1931679>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvsta/23/4?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

[Effects of barrier composition and electroplating chemistry on adhesion and voiding in copper/dielectric diffusion barrier films](#)

J. Appl. Phys. **110**, 044312 (2011); 10.1063/1.3624659

[Modeling self-annealing kinetics in electroplated Cu thin films](#)

J. Appl. Phys. **103**, 113521 (2008); 10.1063/1.2937249

[Effects of residual impurities in electroplated Cu on the Kirkendall void formation during soldering](#)

Appl. Phys. Lett. **92**, 092109 (2008); 10.1063/1.2890072

[Effects of wetting ability of plating electrolyte on Cu seed layer for electroplated copper film](#)

J. Vac. Sci. Technol. A **22**, 2315 (2004); 10.1116/1.1795831

[Effects of a new combination of additives in electroplating solution on the properties of Cu films in ULSI applications](#)

J. Vac. Sci. Technol. A **18**, 1207 (2000); 10.1116/1.582326



Advance your technology or engineering career using the **AVS Career Center**, with **hundreds of exciting jobs** listed each month!

<http://careers.avs.org>



Effect of plating current density and annealing on impurities in electroplated Cu film

Chi-Wen Liu

Department of Applied Physics, National Chia Yi University, Chia-Yi, Taiwan

Ying-Lang Wang^{a)}

Department of Applied Physics, National Chia Yi University, Chia-Yi, Taiwan and College of Science and Engineering, National University of Tainan, Taiwan

Ming-Shih Tsai

National Nano Device Laboratories, Hsinchu, Taiwan

Hsien-Ping Feng

Taiwan Semiconductor Manufacturing Company, Ltd., Hsinchu, Taiwan

Shih-Chieh Chang and Gwo-Jen Hwang

College of Science and Engineering, National University of Tainan, Taiwan

(Received 27 November 2004; accepted 18 April 2005; published 21 June 2005)

This study uses secondary-ion-mass spectrometry to examine the effects of plating current density and annealing temperature on the nature of electroplated copper (Cu) films. The experimental results reveal that high levels of impurities, such as C, O, S, and Cl, are incorporated into Cu deposits at the lower current density region while superfilling occurs. The C and O impurities can be released from the plated films by thermal annealing, while S and Cl cannot. This work proposes a possible mechanism based on bond strength to explain the phenomena. Rapid C and O desorption is observed when the films are first cycled to 220 °C immediately after electroplating. The activation energy of C desorption is found to be approximately 9.8 kJ/mol. For Cu electroplating, this investigation suggests that high plating current density and an adequate annealing temperature are required to reduce impurities. © 2005 American Vacuum Society. [DOI: 10.1116/1.1931679]

I. INTRODUCTION

For application to multilevel metallization in ultralarge-scale integrated circuits, the most highly used materials, aluminum (Al) and its alloys, suffer from the problems of high resistance-capacitance delay, limited electromigration (EM) resistance and poor stress-migration resistance. In comparison to Al, copper (Cu) is more electrically conductive and can achieve higher operating frequencies and lower power consumption. Moreover, Cu is heavier than Al and has higher EM resistance under a current density up to 10^9 A/cm². Higher resistance to stress-induced voiding or open circuits in their metallic interconnects is also achieved by proper use of Cu.¹

By decreasing the feature size, the semiconductor industry faces an increasingly difficult challenge in establishing void-free conductor lines. Voids that will cause reliability problems are generated easily in vias and lines during metal deposition. Electroplating is currently the method of choice to obtain void-free Cu interconnects due to its excellent gap-filling capability. The bottom-up characteristic can be achieved by selected additives dispersed in acidic Cu sulfate electroplating baths.¹⁻⁸

Our superfilling technology with special additives for plating bath formation is designed to enable effective gap filling in high-aspect-ratio vias and lines, but does not ad-

dress the issues for low impurity incorporation. Consequently, an improved plating method for forming Cu interconnects is needed to enhance gap-filling capability as well as to reduce film impurities.

Notably, many researchers have reported that the addition of impurities decreased as the plating current was increased.² However, this study found that the quantity of various impurities is not simply proportional to the plating current density. In addition, the annealing process may significantly influence impurity uptake. After electroplating, the deposited films are usually subjected to further annealing to remove weak-bonded impurities, and thus form larger grains and minimize the number of grain boundaries in the Cu layer.^{9,10} This work discusses the effects of plating current densities and annealing temperatures on the impurity incorporation in the electroplated Cu films.

II. EXPERIMENT

In this work, a 400 nm thick SiO₂ was grown on the bare Si wafers by thermal oxidation. Before Cu electroplating, a sputtered 30 nm TaN/Ta barrier layer and then a 150 nm sputtered Cu seed conduction layer were deposited on the blanket oxide wafers. Cu electroplating was performed on 8 in. Si (100) wafers using a sulfate based plating bath containing CuSO₄·5H₂O (50 g/l), H₂SO₄ (20 g/l), chloride ions (80 ppm), polyalkylene glycol (ethylene oxide and polypropylene oxide copolymers with molecular weight ranging from 2000 to 8000 g/mol obtained from Shipley)

^{a)}Author to whom correspondence should be addressed; electronic mail: ylwang@tsmc.com

(15 ml/l), and bis(3-sulfopropyl) disulfide (5 ml/l obtained from Shipley). The bath temperature was maintained at 25 ± 1 °C using a heat exchanger, and the current density was varied from 10 to 60 mA/cm².

To accelerate impurity liberation from the Cu films, the as-deposited films were annealed with various temperatures of 100, 180, and 220 °C. The annealing ambient contains 96% N₂ and 4% H₂ to prevent Cu film oxidation. The annealed specimens then were furnace cooled. Secondary ion mass spectrometry (SIMS) using the mass of Cu atom as a reference was employed to characterize the deposits and clarify the impurity correspondence to plating current density and annealing. The defect images of plated Cu films were investigated by scanning electron microscopy and transmission electron microscopy.

III. RESULTS AND DISCUSSION

A. Effect of plating current density on impurity levels of electroplated Cu film

The impurities incorporated into the Cu films are determined by the adsorption or desorption behaviors of the breakdown/oxidized species on plated surfaces. Increasing current density has been observed to reduce the concentration of various impurity elements in the plated Cu films, such as carbon and sulfur.² In this study, a lower current density is performed first on the Cu seed to facilitate the void-free filling, then a higher current density is supplied to increase the deposition rate for throughput improvement.

In this experiment, the Cu layers are electrodeposited by three steps with current densities of 10, 40, and 60 mA/cm², respectively. The additives are partially consumed during electroplating. To maintain mass transport control of the additives, the adsorbates must either be included in the growing film or undergo reductive desorption during Cu deposition.

Figure 1 shows the secondary ion counts of additive-derived impurities (carbon, chloride, sulfur, and oxygen) against sputtering time. According to Faraday's second law,¹¹ the mass of Cu liberated in the electrolyte is proportional to its chemical equivalent weights, i.e., the growth rate of electrodeposits is constant for fixed plating current density. Therefore, the mass or thickness per unit area of Cu electrodeposits can be obtained through the plating time multiplied by the current density. In the SIMS plot of Fig. 1, the plated film thickness is proportional to the sputtering time. The time intervals of 100, 200, 350, and 400 s are associated with the I60, I40, I10, and Cu seeds, respectively. (Herein I10: 10 mA/cm²; I40: 40 mA/cm²; and I60: 60 mA/cm².)

From Fig. 1(a), the carbon concentration in the Cu films decreases with increasing current density. During the plating, PEG-Cl complexes act as the inhibitors while organo-sulfide compounds are used as the accelerators. Carbon impurities may come from organo-sulfide compounds during electroplating. It was suggested in the prior research that PEG would not be included in the plated film.⁴ In addition, previous studies¹ have indicated that Cu does not form a stable compound with carbon, and thus presumably the trapped car-

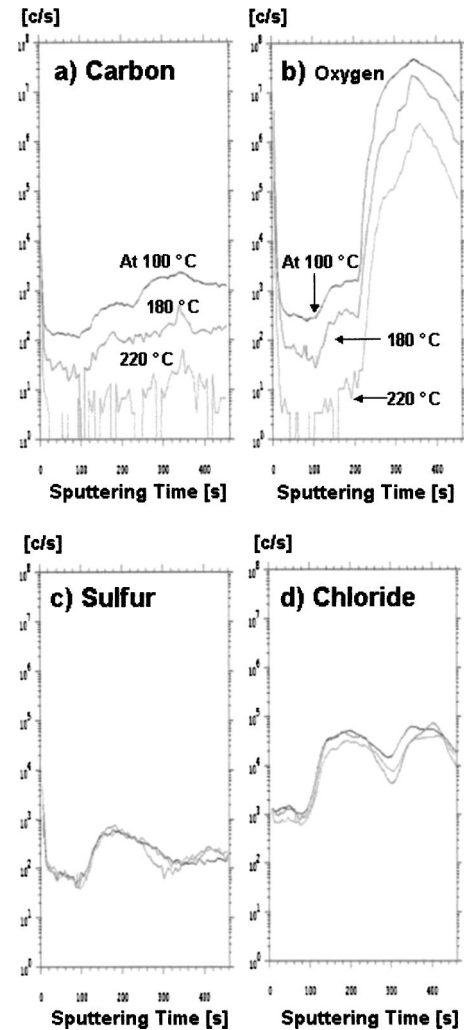


Fig. 1. Depth profile analysis of SIMS spectra obtained from various electroplating current densities (herein the time intervals of 100, 200, 350, and 400 s are associated with I60, I40, I10, and Cu seed, respectively) and the three annealing temperatures (herein top curve: 100 °C; middle curve: 180 °C; and bottom curve: 220 °C). Secondary ion counts for (a) carbon, (b) oxygen, (c) sulfur, and (d) chloride are plotted against sputtering time.

bon can be removed easily from the deposits through external thermal energy, as discussed in the following sections.

Figure 1(b) reveals that the oxygen incorporation into the deposits decreases from I10 to I60 regions, indicating that the incorporation of O²⁻ ions into the Cu electrodeposits correlates strongly with the current density. Additionally, a large amount of oxide exists at the surface of the Cu seed owing to ambient oxidation before electroplating.

From Fig. 1(c), sulfur signals are high for low current density. These high sulfur signals are caused by sulfate in the bulk electrolyte and also possibly by the sulfur groups in organo-sulfide compounds.⁷ On the other hand, the consumption of Cl in the electroplating process recently was investigated by the observation of depth profiles of Cl concentration in the electroplated Cu.⁵ The Cl contents are compatible in the Cu films deposited by I10 and I40, as shown in Fig. 1(d).

The impurities in the Cu electrodeposits with various plating current densities were characterized by SIMS depth profile analysis. The analytical results demonstrate that the amounts of impurities, comprising C, O, S, and Cl, vary with the plating current density. The impurity incorporation into the Cu deposits is lower at the higher plating current density region, i.e., the higher Cu deposition rate. This phenomenon implies that the incorporation of impurities into Cu films is not directly related to the electrochemical reduction at the cathode, but rather must be conducted by diffusion control.

Tan and Harb⁸ determined that superfilling in high-aspect-ratio recess depending on the existence of a long transition time for depolarization was related to the organo-sulfide additives. Superfilling would take effect at the lower Cu deposition rate that achieves sufficient response time for additive adsorption. This phenomenon explains the high levels of S and Cl impurities in the Cu deposits at the current densities of 10 and 40 A/cm². Otherwise, at high current density of 60 A/cm², the Cu deposition rate is faster than the additive adsorption, meaning superfilling hardly occurs due to the lack of effective additive adsorption. Furthermore, Chang *et al.*³ proposed that too low plating current density generated porous films with higher defect density but the defects in porous films could be reduced by increasing the plating current densities. This phenomenon again explains the reducing dependence of impurity levels on increasing the current density.

Impurities in the electrodeposits significantly affect the quality of electroplated films. The impurity incorporation easily induces numerous defects, such as interface discontinuity between the deposited Cu and barrier metal [see Fig. 2(a)], and corrosion voids in conductor lines with high pattern densities [see Fig. 2(b)]. Those interface discontinuities or voids would cause device failure or burn-in. Previous studies also reported that the trapped impurities, such as SO₄²⁻ and Cl⁻ in Cu films deposited by electroless or electroplating, easily cause severe corrosion.

Identification of the degree to which various species incorporated in the film is important, as mentioned above. However, the adsorption behavior and the desorption reaction of various species are closely related to numerous factors, including species types, ion drift, ion diffusion, consumption of ions in the electrolyte, decomposition, and interplay among the additives.⁴⁻⁸ The analysis is very complex. Further study of this area is required in the future.

B. Effect of annealing on impurity levels of electroplated Cu film

Impurity uptake in the plated film can be reduced by external annealing, which frequently is performed to recrystallize the plated Cu films.^{9,10} As shown in Fig. 1, the SIMS data of the deposited films annealed at various temperatures displays a large amount of information. Both the sulfur and chloride contents remain constant over the examined annealing temperature, but the concentrations of carbon and oxygen decrease with increased annealing temperature, indicating that the C and O is thermally unstable in the deposits.

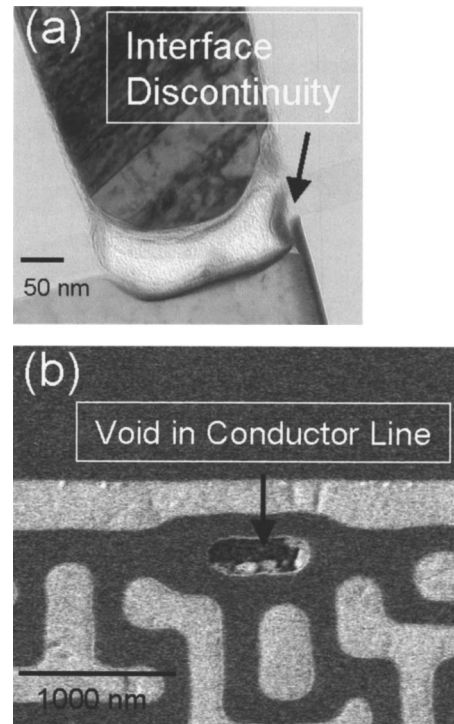


FIG. 2. Examples of defect morphologies in the plating wafer due to incorporation of impurities: (a) TEM image of interface discontinuity between the deposited Cu and barrier metal and (b) SEM image of void in conductor lines.

Carbon is expected to separate from Cu film under annealing because the bond between Cu and carbon is weak. On the other hand, previous works¹ have reported that Cu was oxidized slowly in moist air, and moreover the oxidation rate increased in the presence of acidic gas such as CO₂, leading to the formation of hydroxy carbonate [Cu(OH)₂ CuCO₃]. As expected, the desorption efficiency under heating for these two forms of bonding differs due to diversity in bonding energy. Distinguishing between the Cu–O and the Cu–CO_x bonding effects on the desorption of oxygen from the as-deposited film after annealing treatment remains impossible at this point. Fortunately, the bonding strength of Cu–O (269 kJ/mol) was reported to be almost identical to that of Cu–S (276 kJ/mol),¹ implying that the thermal energy used in this investigation cannot break the Cu–O bonding since the Cu–S bonding is stable, as revealed in Fig. 1(c).

Accordingly a desorption mechanism of C and O in the plated Cu film is proposed in Fig. 3. Prior to annealing, the as-deposited film comprises numerous small Cu grains with some inclusions, which are assumed to be randomly distributed in the film. After annealing, it is thought that the Cu film is recrystallized to form a large grain structure,^{9,10} that C is free, and only O atoms bonded to C can coevaporate with C in the form of CO_x, reducing oxygen incorporation in the films. However, the decay rate of oxygen concentration could not be estimated as was done for carbon, which indicates O cannot only be lost as CO_x. The other oxygen desorption processes are involved, e.g., outdiffusion of free oxygen through the Cu film.

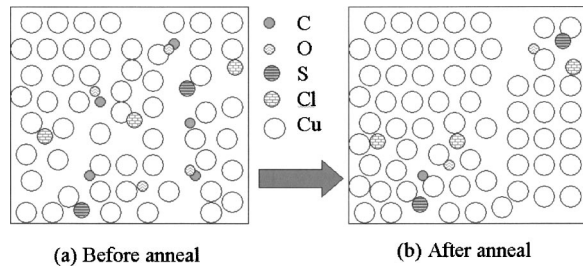


FIG. 3. Proposed desorption mechanism of C and O in the plated Cu film.

Figure 4 illustrates the annealing temperature and time dependence on the liberation of carbon in the plated Cu films. The relative concentration of carbon incorporated in the Cu films is calculated using the following equation, normalized to the numbers of C atoms in the as-deposited films:

$$\text{Relative [C] content(\%)} = N_{\text{C-anneal}}/N_{\text{C-as-deposited}} * 100\% \quad (1)$$

where $N_{\text{C-anneal}}$ and $N_{\text{C-as-deposited}}$ denote the numbers of carbon atoms after annealing and as-deposited, respectively. Clearly, the carbon concentration rapidly drops from 100% to very low trace amounts (smaller than 15%) after 30 s annealing with temperatures of 180 and 220 °C. The decrease in carbon concentration is slower for 100 °C annealing. After 30 s annealing, the carbon content is decreased to 54%. Moreover, after 240 s annealing, the concentration of carbon is decreased to just 20%.

The above results indicate that the desorption rate of carbon may be enhanced significantly by increasing the annealing temperature and/or the time duration. Additionally, the annealing temperature seems to dominate the carbon removal. An increase in the annealing temperature accelerates the removal of removable atoms. This action can reduce the thermal budget of the damascene process, which is important because inappropriate thermal treatment often causes reliability problems in conductor lines and vias.

From the data shown in Fig. 5, the carbon desorption rate increases rapidly with increased annealing temperature. A standard Arrhenius model was used, with carbon concentration versus time data being taken for the three annealing temperatures:

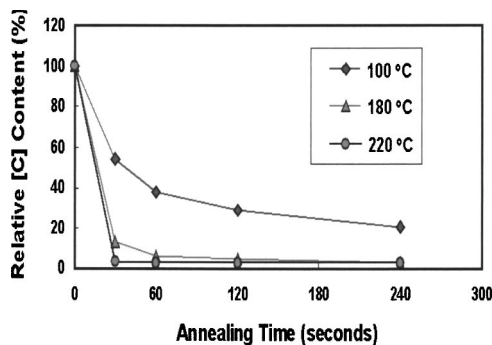


FIG. 4. Dependence of relative carbon contents in the plated Cu films on annealing temperature and time.

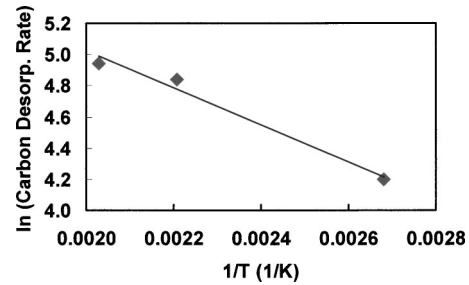


FIG. 5. Dependence of carbon desorption rate in plated Cu films on reciprocal annealing temperature.

$$R(T) = R_0 \exp(-E_a/KT), \quad (2)$$

where $R(T)$ denotes the rate of carbon desorption, monitored by changes in the concentration of carbon in the initial desorption stage (30 s annealing); R_0 represents the frequency factor; E_a is the activation energy, K denotes Boltzmann's constant, and T represents the absolute temperature. The activation energy of carbon desorption calculated from the slope of the straight line in Fig. 5 is around 9.8 kJ/mol for Cu–C bond breaking. The quantity of Cu–C bond breaking is considerably smaller than in the case of Cu–S bond breaking, by a factor of 28, indicating that carbon is released more easily than sulfur in Cu film.

IV. CONCLUSION

The SIMS results described here increase understanding of the effect of plating current density and annealing process on the inclusions in Cu electrodeposits. The experimental results reveal that C, O, S, and Cl from sulfate anions and organic additives are included in the Cu deposits. Moreover, the concentrations of the various impurities are sensitive to the plating current density. Species incorporation increases with decreasing current density due to insufficient time for additive desorption. Furthermore, postelectroplating annealing can release C and O from the plated films, while S and Cl are still strongly bonded in the films after annealing. Since O and S bond to Cu with almost equal energy, this investigation suggests that the O atom bonded to C will corelease with C and the O atom bonded to Cu will be trapped like S. 100 °C annealing reveals incomplete desorption of the film species. The C and O contents can rapidly decrease if the films are first cycled to 220 °C immediately after plating and minimum desorption time is more pronounced for all samples using 220 °C anneal. The activation energy of C desorption is also calculated as being approximately 9.8 kJ/mol. Therefore, to reduce the Cu corrosion and oxidation, a high plating current density and adequate annealing are recommended.

ACKNOWLEDGMENTS

This work was performed at the National Nano Device Laboratory and was supported by Chemat Technology, Inc., USA, and the National Science Council of the Republic of China under Contract No. NSC 91-2721-2317-200.

- ¹S. P. Murarka, I. V. Verner, and R. J. Gutmann, *Cu—Fundamental Mechanisms for Microelectronic Applications* (Wiley, New York, 2000).
- ²S. Gandikota, D. Padhi, S. Ramanathan, C. McGuiirk, R. Emami, S. Parikh, G. Dixit, and R. Cheung, Proceedings of International Interconnect Technology Conference (IITC), 2002, p. 197.
- ³S. C. Chang, J. M. Shieh, B. T. Dai, M. S. Feng, and Y. H. Li, *J. Electrochem. Soc.* **149**, G535 (2002).
- ⁴M. Kang and A. A. Gewirth, *J. Electrochem. Soc.* **150**, C426 (2003).
- ⁵M. Hayase, M. Taketani, K. Aizawa, T. Hatsuzawa, and K. Hayabusa, *Electrochem. Solid-State Lett.* **5**, C98 (2002).
- ⁶M. Hayase, M. Taketani, T. Hatsuzawa, and K. Hayabusa, *Electrochem. Solid-State Lett.* **6**, C92 (2003).
- ⁷A. Frank and A. J. Bard, *J. Electrochem. Soc.* **150**, C244 (2003).
- ⁸M. Tan and J. N. Harb, *J. Electrochem. Soc.* **150**, C420 (2003).
- ⁹Q. T. Jiang and M. E. Thomas, *J. Vac. Sci. Technol. B* **19**, 762 (2001).
- ¹⁰C. Lingk and M. E. Gross, *J. Appl. Phys.* **84**, 5547 (1998).
- ¹¹P. K. Pandey, S. N. Sahu, and S. Chandra, *Handbook of Semiconductor Electrodeposition* (Marcel Dekker, New York, 1996).