



Microstructural Study of the Effect of Chloride Ion on Electroplating of Copper in Cupric Sulfate-Sulfuric Acid Bath

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The purpose of this work is to study the electrocrystallization behavior of the copper deposit on pure titanium substrate. The electroplating was conducted at 0.7 A/cm², 65°C in cupric sulfate-sulfuric acid bath with various chloride additions (45–350 ppm). Initial growth morphology and microstructure of the deposit were examined with a field-emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope integrated with an energy-dispersive X-ray spectrometer. Results of cathodic polarization and galvanostatic plating experiments show that the increasing concentration of chloride ions in the plating bath would significantly increase the cathodic potential. This cathodic potential increase was found to be induced by the presence of CuCl precipitates on the cathodic surface as well as on the copper cluster formed during the electrocrystallization process. At the initial plating stage, both copper and hexagonal-shaped CuCl precipitates were produced simultaneously. Eventually, the pyramid-shaped CuCl precipitates were observed, which consisted of many parallel hexagonal planes stemming from a screw dislocation. The polarization effect of CuCl precipitate on the Ti substrate was further confirmed and clarified. Through measurement of the electrode response and investigation of the deposit using FESEM, it was observed that under identical electroplating conditions, much less CuCl forms on a copper substrate in the initial stages than on a titanium substrate, leading to lower polarization.

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It is well known that adding chloride ions in a sulfuric acid bath for copper electroplating is required to improve the surface brightness and mechanical properties of the deposit.^{1–3} It has been reported that the addition of a small amount of chloride ions (~10 ppm) in an acidified copper plating bath would accelerate the reduction reaction of cupric to cuprous ions. The formation of cuprous chloride^{4,5} or even an insoluble salt film^{6,7} on the cathode surface can increase the polarization. Furthermore, this effect has been observed to increase as the chloride ion concentration in solution rises. However, few studies have been focused on the microstructures of the cuprous chloride and/or the salt film formations.

Some studies^{8–11} have reported that the crystallographic orientation and surface morphology of the copper deposit could be affected by chloride ion addition in the plating bath. It was also recognized that the smaller grain size of the copper deposit could be obtained with an addition of chloride ions.^{1,6,12} Carneval⁹ suggested that the anion could be a complex former or even codeposit with Cu²⁺ during copper deposition. However, changes in the microstructure and the electrocrystallization behavior of the copper deposit relating with the chloride addition were not examined and discussed in the previous literature. In addition, most research^{13,14} on the behavior of the copper plating has been carried out at low temperature and low current density. Several studies^{15–17} reported that the surface morphology and the microstructure of copper deposit could be affected by the electroplating current density. Furthermore, the current density lies in the fraction of the limiting current density that is of concern.^{18,19} Wu et al.²⁰ studied the morphology of copper deposited on a Cu(100) substrate in an acid-sulfate plating solution containing a small amount of HCl at 30 mA/cm²; they found that chloride ions tended to stabilize the Cu(100) surface, and the morphology of copper deposit composed of pure Cu instead of CuCl assumed a square pyramid shape. Yet little is conferred about the effect of the chloride ion on the copper plating at high current density and temperature condition, by which a high copper-deposition rate could be achieved.

With different cathodic substrates and additives, many studies^{21–24} have investigated the growth behavior of the copper deposit with an atomic force microscope (AFM), by which the initial growth morphology of the deposit could be examined in the atomic scale. However, the crystallographic structure of cuprous chloride with respect to copper deposit and their chemical composition

analyses are still unavailable. In this study, the electrocrystallization of copper in a chloride-containing bath on a Ti substrate was investigated with a field-emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM). An energy-dispersive X-ray spectrometer (EDS) was integrated in FESEM as well as HRTEM allowing composition analysis of a particular local region feasible in a size of ca. 5 nm. This study reports in detail the electrocrystallization of the copper deposit and cuprous chloride precipitation in a chloride-containing bath. In order to clarify the cathodic polarization effect caused by CuCl precipitates, the copper deposition experiments on a Cu substrate were also conducted and studied in comparison with that obtained on a Ti substrate.

Experimental

A rotating cylinder electrode (RCE), fabricated from pure titanium (99.5 wt %, grade 2) with an exposed area of 1.0 cm² (8.4 mm in diameter and 4 mm in length), was used as the cathode. The copper electroplating was performed in a conventional acid bath composed of CuSO₄·5H₂O (90 g/L) + H₂SO₄ (120 g/L) with addition of chloride ions ranging from 45 to 350 ppm. The copper electroplating was conducted at 0.7 A/cm², 65 ± 0.5°C. The rotation speed of RCE was kept at 2000 rpm using a rotating disk-cell kit (EG&G RDE 0001). A platinized Ti-mesh and Ag/AgCl_(sat) were used as counter and reference electrodes, respectively. Because leakage of a small amount chloride ions into the electroplating bath could possibly disturb the deposition behavior when the Ag/AgCl reference electrode was used, the potential difference between Ag/AgCl and SCE reference electrodes was carefully measured before and after some electrochemical experiments. The recorded data showed that the variations of the potential difference were within 5 mV; that is, the disturbance caused by using the Ag/AgCl reference electrode is relatively small.

The cathode Ti-surface was mechanically ground to 1200 grit finish, cleaned in acetone, and dried with cold air for copper electroplating. Cathodic polarization curves were measured from open-circuit potential to –1500 mV (vs Ag/AgCl_(sat)) at 10 mV/s. To eliminate the effect of dissolved oxygen, nitrogen purging of the electrolyte for at least 5 min before and during the experiments was performed. Before cathodic polarization measurement, the RCE was immersed in the bath for 15 min until a stable condition was established between the RCE and the plating electrolyte. Employing the same preparation condition and electroplating system as those used in the cathodic polarization measurement, the cathodic potential was

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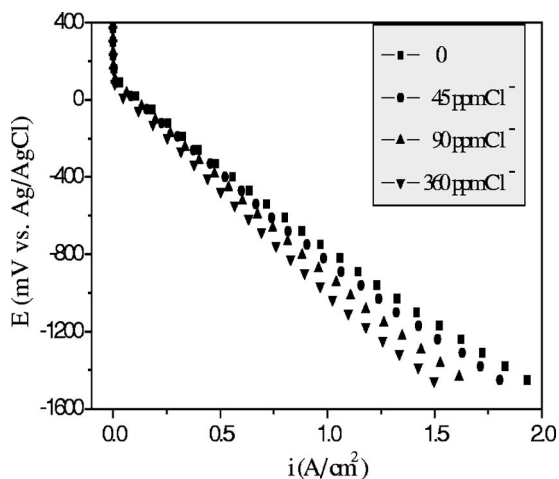


Figure 1. Cathodic polarization curves during copper electroplating at 65°C in sulfuric acid solutions containing different Cl^- concentrations.

measured for 135 s with a plating current density of 0.7 A/cm^2 . The plating current density was about 70% of the limiting current density and this percentage was widely used for high deposition rate copper-electroforming and copper-foil production.²⁵

Galvanostatic copper depositions for different short periods (0.1–10 s) were performed to observe the initial growth morphology. After deposition, the copper deposit on the cathode surface was carefully immersed in an acetone bath, and then dried in the air for FESEM (Hitachi S-4700) further examination. A HRTEM (Philips, CM200) integrated with EDS for chemical composition analysis was used to study the effect of chloride ions on the microstructure of the copper deposit. In order to study the initial growth behavior, the carbon-extraction method for TEM specimen preparation was used to extract the copper deposit for 0.1 s. A Ni mesh of 3 mm diameter was used to hold the carbon film, by which the copper deposit was extracted directly from the RCE surface for TEM examination. Two types of plane-view TEM specimens, made from the innermost and outermost portions of the 5- μm -thick copper deposit, were prepared using single-jetting of both faces of the stripped deposit. The two plane-view TEM observations are expected to shed light on the initiation growth behaviors of copper and cuprous chloride. A pure copper specimen (99.9 wt%) was also employed as a substrate for Cu-deposition experiment with a similar pretreatment as that employed on the Ti substrate.

Results and Discussion

Cathodic polarization test.—Figure 1 shows the cathodic polarization curves of the RCE in the copper plating bath with various chloride concentrations. All cathodic polarization curves lie in the charge-transfer controlled Tafel region in the applied cathodic potential. The cathodic potential was raised obviously with increasing chloride ions at the same current density in the corresponding polarization curves.

As shown in Fig. 2, the cathodic potential was measured during galvanostatic plating (at 0.7 A/cm^2) for 135 s in various chloride-containing copper baths. As expected, the cathodic potential increased with an increase of chloride content. In the absence of chloride, the cathodic potential was about -390 mV; with a 45 ppm chloride bath, the cathodic potential was raised to -490 mV, and to -580 mV with a 360 ppm chloride bath (Fig. 2b). The cathodic potential was relatively stable during galvanostatic plating. It seems that the polarization effect of chloride ions on the cupric reduction maintained throughout the whole electroplating period.

Nagy et al.²⁶ reported that the adsorption of chloride ions at the initial nucleation stage of copper deposit would decrease the overpotential of mass transport. Kelly et al.² studied the copper deposition in an acid bath containing 50 ppm Cl^- by quartz crystal microbalance (QCM). From their results, the chloride ion would accelerate the copper deposition reaction and decrease the cathodic potential. Goldbach et al.⁴ also confirmed its depolarizing effect and the negligible hindrance of CuCl film to charge transfer. In this study, the obvious polarization effect of chloride ions on copper deposition was detected. Upadhyay²⁷ and Holzle²⁸ suggested that the polarization effect could possibly be induced by precipitation of the salt-film and/or adsorption of Cu-TU complexes at the cathodic surface, which might block the active site and result in an increase of cathodic potential with an increase of TU content. The initial growth morphology of copper deposit and CuCl precipitates was thus examined in detail with FESEM and HRTEM in this study such that more light would be shed on this arguing point.

Growth morphology of the copper deposit.—Figure 3 shows the initial growth morphology of copper and cupreous chloride deposits electroplated for 0.1 s at different magnifications. Two distinct features, i.e., many-copper cluster and isolated cupreous chloride triangle, could be obviously found on the cathodic surface, which still reveals some grinding marks on the Ti substrate. Both features were simultaneously developed on the cathodic surface at the very early nucleation stage after 0.1 s (Fig. 3a). With increasing plating time, the copper clusters grew further, whereas the size and shape of CuCl precipitates seemed to remain unchanged (Fig. 4a and 5). It is also depicted evidently that the CuCl precipitates occurred on the

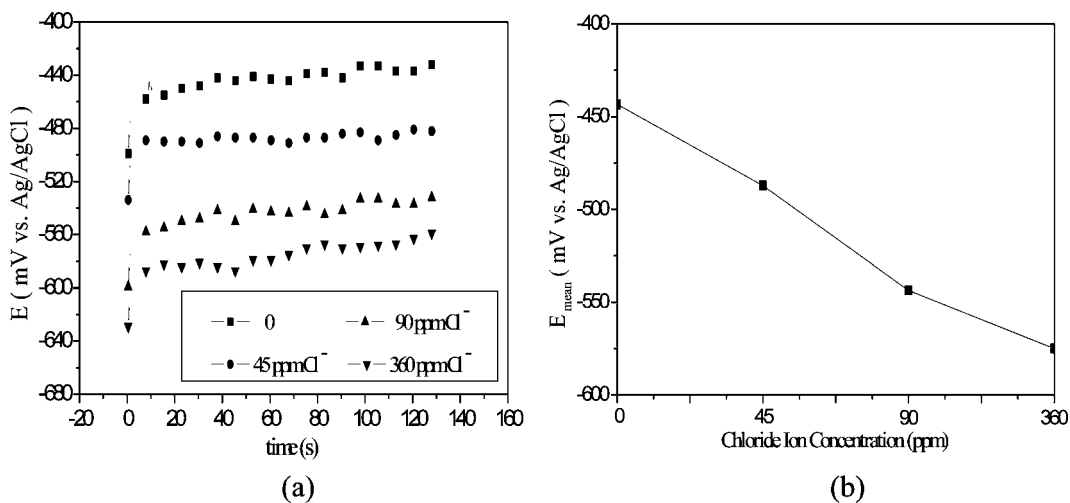


Figure 2. (a) Cathodic potentials monitored during galvanostatic plating at 0.7 A/cm^2 on a Ti substrate. (b) Effect of Cl^- concentration in solution on cathodic potential after 135 s of galvanostatic plating at 0.7 A/cm^2 .

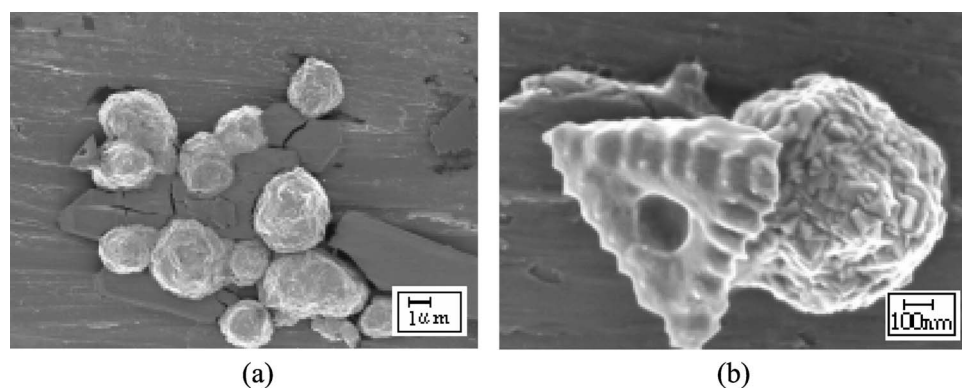


Figure 3. SEM micrographs showing the copper cluster and cupreous chloride triangle after electroplating for (a) 0.1 s and (b) magnified micrograph of (a).

surface of the copper cluster (Fig. 4a). This demonstrates that the CuCl not only precipitated directly on the cathodic titanium surface but was also codeposited with copper.

The greater the chloride addition in the plating bath, the richer the CuCl being precipitated on the cathodic surface, thus causing the higher Tafel slope (or higher charge-transfer resistance) in the cathodic polarization curves (Fig. 1). As shown in Fig. 4a, laterally grown flat copper deposit could also be found adjacent to the copper cluster when the plating period is prolonged. The EDS analysis of A in Fig. 4a (Fig. 4b) shows a relatively intense chlorine peak as compared with that of the negligible chlorine peak of B in Fig. 4a (Fig. 4c); this result proved that the “A” triangle may quite possibly be composed of CuCl precipitate and the “B” plateau may be composed of Cu deposit. Figure 5 shows the appearance of the deposit after electroplating for 10 s. As expected, both cluster and laterally grown flat Cu deposits were observed and the dispersed CuCl precipitates could also be found.

Fabricius²⁹ recognized that CuCl could be precipitated readily on the copper surface due to the formation of insoluble CuCl in a low NaCl concentration bath and soluble cuprous complexes in a high NaCl bath. In this study, few CuCl precipitates were observed on the

cathodic surface without applying cathodic current in the electrode, and the CuCl precipitate was found only on the cathodic charged electrode surface. The cathodic current, therefore, is essential for the production of CuCl precipitate. In addition, continuous, planar salt-film composed of cupreous chloride was not found on the cathodic surface under the selected electroplating condition. Based on the above results, it is suggested that the formation mechanism of CuCl could be as follows: the Cu^{2+} ion acquires an electron at the cathodic surface, forming an adsorbed Cu^+ ion. The adsorbed Cu^+ ion was chemically bonded with a chloride ion in the electrolyte to form CuCl nuclei on the cathode surface because the chloride ion has extra electron pairs and the Cu^+ ion has empty orbitals. The initial nucleation and growth of CuCl on the copper cluster was no surprise because the growing copper deposit was conductive and can act as a cathodic surface.

The microstructure of CuCl precipitates.—Although it was assumed that all the CuCl precipitates assumed triangular shape at lower magnification (Fig. 3), pyramid-shaped CuCl precipitate was observed in the FESEM micrograph with a higher magnification, as shown in Fig. 6a (plating time 1 s). Interestingly, the CuCl pyramids were comprised of many stacked parallel planes, and each plane was composed of many hexagonal-shaped elements. Moreover, a trace of screw dislocation was found in the uppermost plane of the CuCl pyramid. Hence, a planer growth mode of the CuCl precipitate with the aid of screw dislocation, which minimized the growth energy barrier, was postulated. The EDS analysis for this pyramid (Fig. 6b) proved that the possible constituent for the pyramid was CuCl.

HRTEM micrographs of the copper deposits, with and without chloride addition, adjacent to the cathode Ti surface were shown in Fig. 7 and 8, respectively. In the absence of chloride in the plating

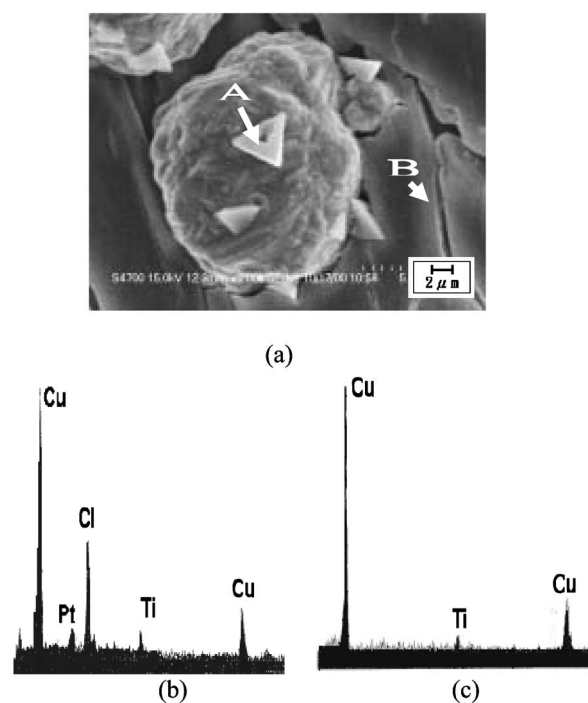


Figure 4. (a) SEM micrographs showing the copper cluster and cupreous chloride triangle after electroplating for 3 s, (b) EDS analysis on point A in (a), and (c) EDS analysis on point B in (a).

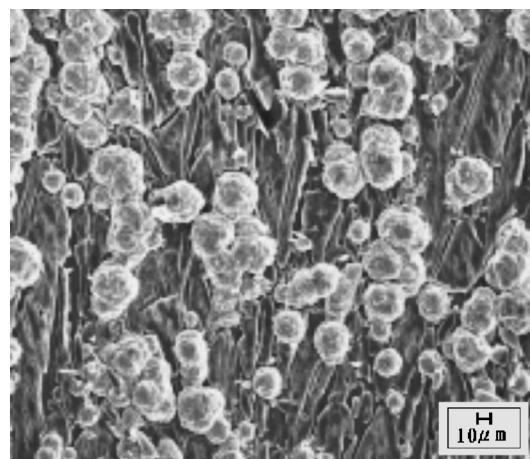


Figure 5. SEM micrographs showing the morphology of copper deposit after electroplating for 10 s in the presence of 45 ppm Cl^- .

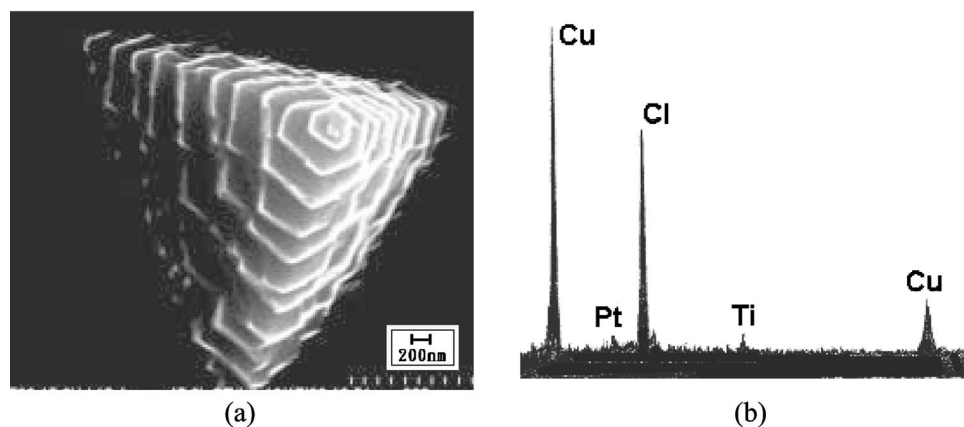


Figure 6. (a) FESEM micrograph showing the pyramid-shaped CuCl after electroplating for 1 s at higher magnification, (b) the EDS analysis of the pyramid CuCl.

bath, no CuCl precipitate was detected in the lattice micrograph of the copper deposit (Fig. 7), which also shows the 1.27 \AA d_{220} spacing of the copper deposit. Some CuCl precipitates, which show apparent moiré interference images and have a hexagonal shape with crystal sizes smaller than 10 nm, were identified as outlined in the specimen plated in the 360 ppm chloride copper bath (Fig. 8). From the pyramid shape of CuCl shown in Fig. 6, it is reckoned that the hexagonal form of CuCl in the TEM micrograph (Fig. 8a) could be the constituent of each pyramid plane. Figure 8b outlines the hexagonal CuCl precipitates in the TEM micrograph of Fig. 8a. From the result of EDS analysis of A, as shown in Fig. 8a (Fig. 8c), the moiré image was mainly composed of chlorine and copper, as compared with that of the copper peak and the negligible chlorine peak of B, as shown in Fig. 8a (Fig. 8d). The moiré image resulted from the interference of different crystallographic diffractions and lattice constants between CuCl and copper. Because moiré images of the CuCl, in the HRTEM micrograph, were distributed randomly in the Cu substrate (Fig. 8), it can also be recognized that there is little crystallographic relationship between CuCl and the Cu substrate.

For more precise confirmation of the presence of CuCl precipitates at the very initial stage of plating, the deposits were directly extracted from the Ti cathode surface with a replicating film. A carbon extraction method was then employed to extract deposits plated for very short time (0.1 s). The result of the HRTEM micrograph was presented in Fig. 9a. As expected, high-density precipi-

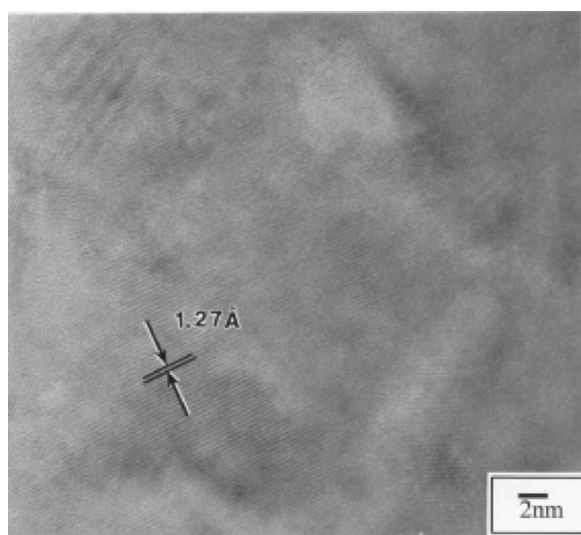


Figure 7. HRTEM image of deposit formed in the absence of Cl^- . The plane in the image is located at the inner surface of the coating adjacent to the Ti substrate.

tates of possibly CuCl composition with crystal sizes about 3-20 nm, can be detected in the initial growth stage of deposition. The diffraction pattern of the precipitate was inserted in Fig. 9a. The cubic crystal structure of the precipitate agreed with that of the CuCl structure (JCPDS PDF no. 30-0472). Furthermore, the particle size of CuCl varied in the range of 5-20 nm. Figure 9b shows the higher magnified HRTEM micrograph of the extracted deposit with a size of 7 nm. It can be seen that a single CuCl precipitate in hexagonal shape with clear lattice images was presented in the micrograph; the 1.71 \AA d_{220} spacing complied well with that of CuCl. Furthermore, it can be clearly observed in Fig. 9b that the (220) planes for CuCl precipitates are parallel to each hexagonal edge. Figure 9c, which shows the micrograph viewed from different angles of that in Fig. 9b, also illustrates that the CuCl precipitates are virtually composed of stacked hexagonal layers. Comparing Fig. 9a with Fig. 4a, it is apparent that the density of the CuCl precipitate is much higher on the titanium surface than that within the copper clusters. This implies that the CuCl precipitate would be more likely to form on the Ti cathode surface than on the Cu deposit, and that many embryo CuCl precipitates terminate their growth as deposition is prolonged.

The HRTEM micrograph of the deposit with the thickness of $5 \mu\text{m}$ from the Ti-substrate surface was shown in Fig. 10; the hexagonal CuCl precipitates were also found and outlined in the deposit electroplated in the copper bath containing 360 ppm chloride. In other baths with various chloride contents, the same observations were obtained. In Fig. 4a, using the FESEM technique, it is observed that CuCl can precipitate on the copper cluster and also exists within the copper deposit. Although CuCl precipitates could be observed on the surface with the thickness of $5 \mu\text{m}$ from the Ti-substrate surface (Fig. 10), the density of CuCl here is significantly lower than that in the deposit adjacent to the Ti-substrate surface (Fig. 8). This implies that CuCl would be more likely to precipitate on the cathode Ti-substrate surface than on the Cu deposit. Interestingly, an obvious size difference of CuCl precipitates was observed with HRTEM and FESEM. The sizes of CuCl precipitates are only ca. 5-10 nm observed by HRTEM (Fig. 8a), but ca. 1-5 μm by FESEM (Fig. 4a). Because the TEM specimen was prepared from the portion of deposit adjacent to the Ti cathode, CuCl nuclei could be observed and, therefore, a high density of CuCl precipitate in nanometer size was registered. The result of the CuCl precipitates in micrometer sizes as observed with FESEM (Fig. 4a) suggests that only a few of the CuCl nuclei can grow during further electrocrystallization. Consequently, the density of CuCl precipitates on the Ti-substrate surface appears much higher than that within the copper deposit.

The polarization effect of CuCl precipitates.—In this study, we confirm that CuCl would be more likely to precipitate on the Ti cathode, leading to an increase of cathodic potential for copper deposition. In addition, a few CuCl precipitates were found within the copper deposit. Because several studies^{2,4,26,30,31} reported that

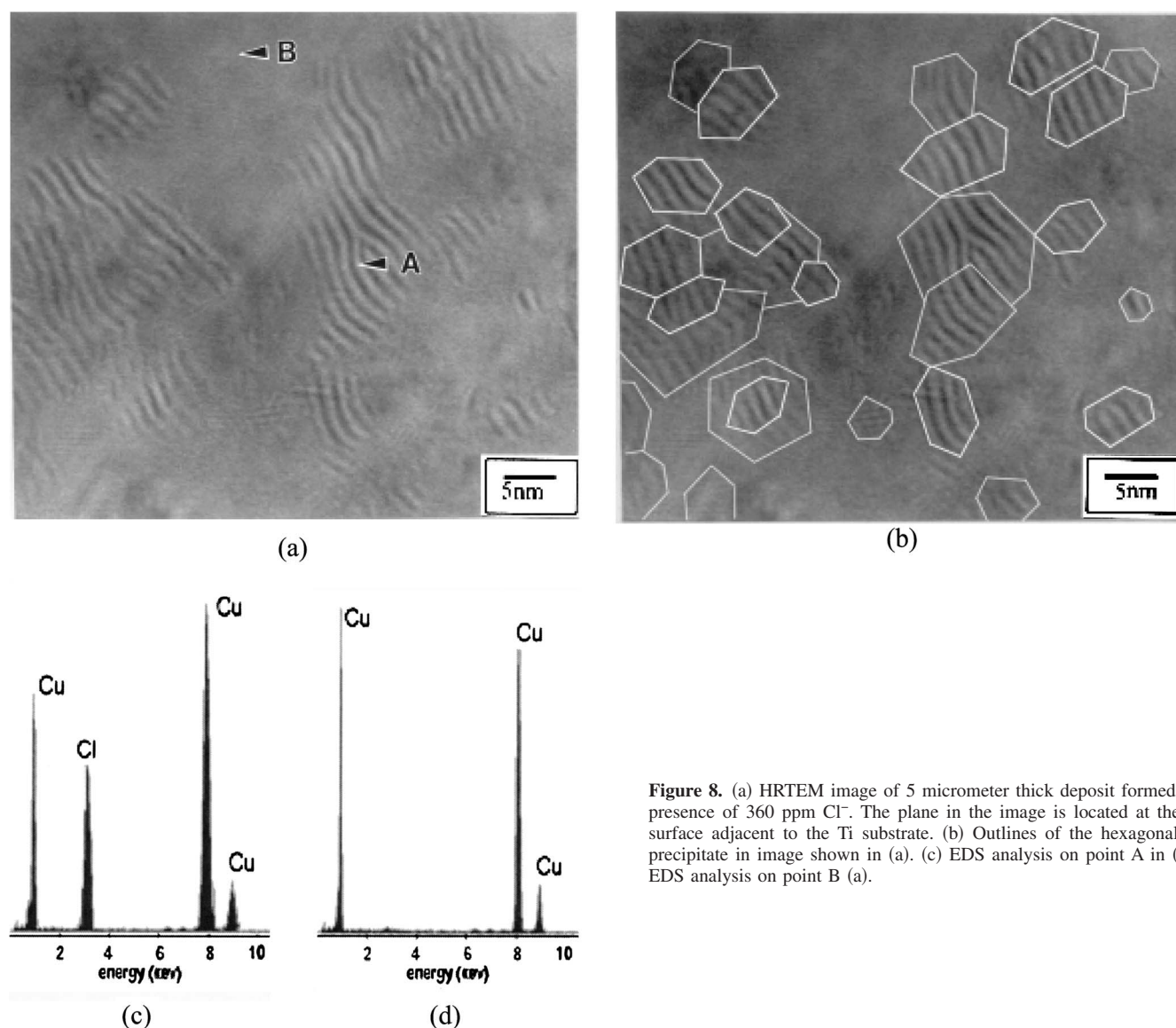


Figure 8. (a) HRTEM image of 5 micrometer thick deposit formed in the presence of 360 ppm Cl^- . The plane in the image is located at the inner surface adjacent to the Ti substrate. (b) Outlines of the hexagonal CuCl precipitate in image shown in (a). (c) EDS analysis on point A in (a). (d) EDS analysis on point B (a).

the addition of chloride ions in the copper plating bath could accelerate copper deposition and decrease the cathodic potential. We, therefore, experimented further using pure copper instead of titanium cathodes for copper deposition to elucidate the difference in the polarizing effect. Figure 11 shows the effect of chloride addition on cathodic potential during galvanostatic deposition at 0.7 A/cm^2 , 65°C for 135 s. Compared with the result of Fig. 2, the cathodic potential of copper deposition on the pure Cu cathode decreased to a large extent with the addition of 45-360 ppm chloride ions in the copper plating bath. This demonstrates that the effect on the polarization by chloride addition depends strongly on the type of substrate for copper deposition.

Concerning the above result, the addition of chloride in a cupric sulfate-sulfuric acid bath seems to play an uncertain role; this prompts us to conduct further FESEM evaluation of CuCl precipitated on Ti and Cu substrates. Figure 12a and b shows the morphology and the amount of chloride precipitated with copper after galvanostatic deposition on Ti and Cu substrates for 0.5 s, respectively. As can be seen clearly, the deposition rate of cupreous chloride on the pure Ti substrate appears much faster than that on the Cu substrate. Abundant CuCl precipitates could be observed on the Ti substrate in Fig. 12a (with 45 ppm chloride content). However, many fewer CuCl precipitates were found on the Cu substrate with much

higher chloride content (with 350 ppm) (Fig. 12b). Summarizing the results of Fig. 2, 11, and 12, it can be concluded that the many fewer CuCl precipitates on the Cu substrate caused the weaker polarization effect of copper deposition. Nonetheless, one question may be raised concerning prolonged plating on the Ti substrate. Once deposition has continued long enough and the Ti substrate is fully covered by copper, one may expect the polarization to decrease toward what is observed on a Cu substrate. The polarizations shown in Fig. 2 after 135 s, however, do not decrease correspondingly to lower values as ratiocinated above. This peculiar behavior implies possibly that the earlier deposited CuCl salt as well as possibly the retained surface TiO_2 still maintain their effects on the cathodic potential of prolonged plating on the Ti substrate. The cathode potential is comprised of basically three portions, namely surface TiO_2 with earlier deposited CuCl and Cu resistances, later plated purer Cu resistance, and Cu/electrolyte charge-transfer resistance. Consequently, more detailed study is required to analyze the peculiar behavior, and the work is in progress.

Based on the results of Fig. 11 and 12, it is suggested that the initial growth mode and $\text{Cu}^{2+}/\text{Cu}^+$ complex reaction catalyzed effectively by trace amounts of chloride ions in the copper bath. The catalyst effect, as proposed by Nagy et al.,²⁶ tended to enhance the

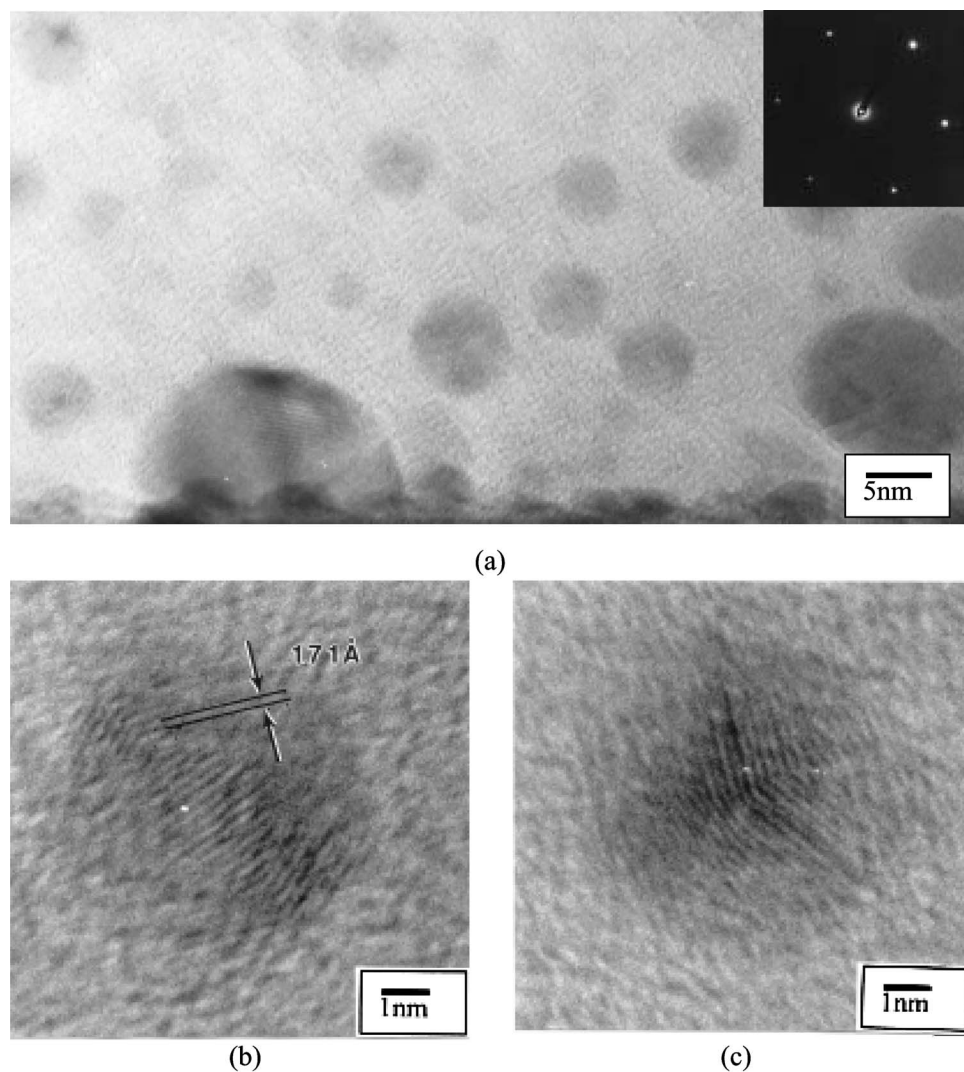


Figure 9. (a) HRTEM image showing distribution of CuCl that has been carbon-extracted from Ti surface. (b) HRTEM image of (a) at higher magnification. (c) Lattice image micrograph of (b) viewed from a different angle.

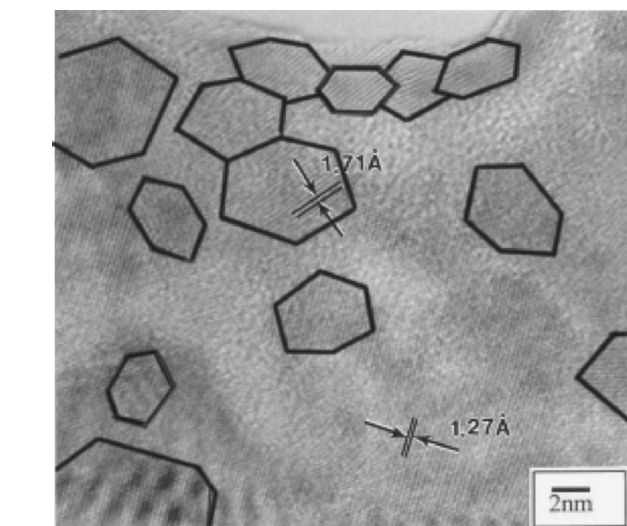


Figure 10. HRTEM image showing an outline of hexagonal CuCl enclosed within copper deposit formed in the presence of 360 ppm Cl^- . The plane in the image is located 5 micrometers from the Ti substrate surface.

rate of Cu^{2+} reduction due to the formation of a bridge between Cu^{2+} and Cl^- with a shorter spacing in the presence of chloride ions than that of $\text{Cu}^{2+}/\text{H}_2\text{O}/\text{metal}$ bridges in a chloride-free system. For

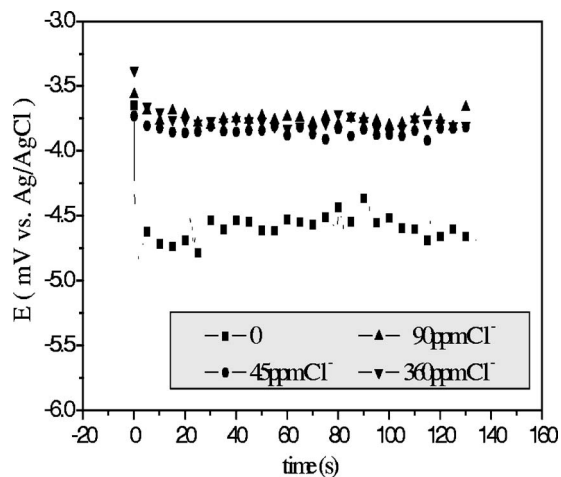
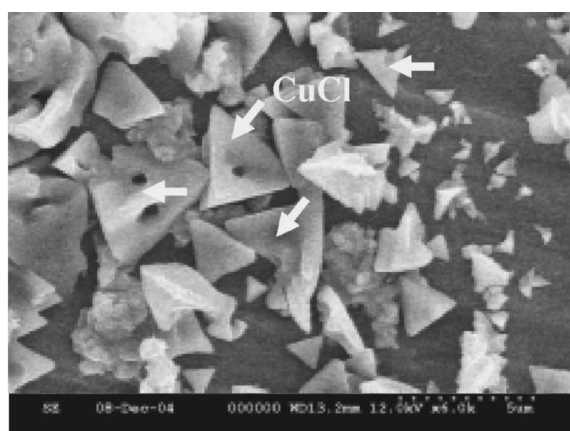


Figure 11. Cathodic potential monitored during copper electroplating at 65°C on a copper substrate in sulfuric acid solution containing different Cl^- concentrations.



(a)



(b)

Figure 12. FESEM micrograph showing the morphology and the amount of CuCl precipitated with copper deposit on (a) Ti substrate (45 ppm Cl^-), (b) Cu substrate (360 ppm Cl^-) after galvanostatic plating for 0.5 s.

general application in industrial baths, the chloride content varies from 50 to 100 ppm and the depolarizing effect of copper deposition on the Cu substrate was also reported.⁴ In these plating cases, a low coverage of CuCl or salt film on the cathode and low hindrance of charge transfer across the interface of the cathode/electrolyte was reported. However, the presence of adsorbed molecules, such as long chain PEGs, LP-1, and Cl-complexes, would also reduce the active sites leading to the cathodic potential increase of copper deposition.^{4,32,33} In this study, we confirm the presence of abundant CuCl precipitates on the Ti cathode but only a few CuCl being encapsulated within copper deposit in the chloride containing copper bath. High-density inert CuCl precipitates on the Ti cathode would theoretically decrease the active sites of the cathode surface for copper deposition and result in the significant polarization effect of copper deposition.

Conclusions

The effect of chloride ions on electrocrystallization of copper plated at 0.7 A/cm², 65°C on a Ti substrate was studied. The addi-

tion of chloride ions in the copper plating bath would cause the formation of high-density precipitation of CuCl on the Ti cathode surface, and much less CuCl precipitate on the as-plated copper cluster. The CuCl precipitation would lead to higher charge-transfer resistance for cupric ions reduction on the cathode. The more chloride ions added in the plating bath, the higher the cathodic potential is required during galvanostatic plating. From the FESEM and HRTEM examinations, it can be seen clearly that copper cluster and hexagonal CuCl precipitates were produced simultaneously at the initial plating stage. The stacking of parallel planes, with each plane comprising many hexagonal CuCl units at a later growth stage, leads to the formation of pyramid-shaped CuCl precipitates. These FESEM and HRTEM examinations explain that the pyramid-shaped CuCl precipitates were possibly originated and grown with the aid of screw dislocations.

The polarization effect of CuCl precipitates on the Ti substrate was further confirmed and clarified. Through measurement of the electrode response and investigation of the deposit using FESEM, it was observed that under the identical electroplating condition, much less CuCl forms on a copper substrate in the initial stages than on a titanium substrate, leading to lower polarization.

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References

- W. H. Gauvin and C. A. Winkler, *J. Electrochem. Soc.*, **99**, 71 (1952).
- J. J. Kelly and A. C. West, *J. Electrochem. Soc.*, **145**, 3472 (1998).
- A. V. Benedetti, P. T. A. Sumodjo, K. Nobe, P. L. Cabot, and W. G. Proud, *Electrochim. Acta*, **40**, 2657 (1995).
- S. Goldbach, W. Messing, T. Daenen, and F. Liapicque, *Electrochim. Acta*, **44**, 323 (1998).
- M. Fonsati, F. Zucchi, and G. Trabaneli, *Electrochim. Acta*, **44**, 311 (1998).
- S. Yoon, M. Schwartz, and K. Nobe, *Plat. Surf. Finish.*, **81**, 65 (1994).
- S. Yoon, M. Schwartz, CEF, and K. Nobe, *Plat. Surf. Finish.*, **82**, 64 (1994).
- R. Walker and S. D. Cook, *Surf. Technol.*, **11**, 189 (1980).
- G. Carneval and J. Bebczuk de Cusminsky, *J. Electrochem. Soc.*, **128**, 1215 (1981).
- M. Peykova, E. Michailova, D. Stoychev, and A. Milchev, *Electrochim. Acta*, **40**, 2595 (1995).
- N. Pradhan, P. G. Krishna, and S. C. Das, *Plat. Surf. Finish.*, **March**, 56 (1996).
- P. V. Brande and R. Winand, *Surf. Coat. Technol.*, **52**, 1 (1992).
- F. A. Harraz, T. Sakka, and Y. H. Ogata, *Electrochim. Acta*, **47**, 1249 (2002).
- C. Gabrielli, P. Mocoteguy, H. Perrot, and R. Wiert, *J. Electroanal. Chem.*, **572**, 367 (2004).
- M. Alodan and W. H. Smyrl, *Electrochim. Acta*, **44**, 299 (1998).
- T. J. O'Keefe and L. R. Hurst, *J. Electroanal. Chem.*, **8**, 109 (1978).
- A.-M. Lafront, B. Veilleux, and E. Ghali, *J. Appl. Electrochem.*, **32**, 329 (2002).
- R. Winand, in *Application of Polarization Measurements in the Control of Metal Deposition*, I. H. Warren Editor, p. 47, Elsevier, Amsterdam (1984).
- R. Winand, *Electrochim. Acta*, **43**, 2925 (1998).
- A. Wu and D. P. Barkey, *J. Electroanal. Chem.*, **150**, C533 (2003).
- E. D. Eliadis, Ralph G. Nuzzo, Andrew A. Gewirth, and Richard C. Alkire, *J. Electrochem. Soc.*, **144**, 96 (1997).
- D. Grujicic and B. Pestic, *Electrochim. Acta*, **47**, 2901 (2002).
- Chi-Chang Hu and Chi-Ming Wu, *Surf. Coat. Technol.*, **176**, 75 (2003).
- M. Kang and A. A. Gewirth, *J. Electrochem. Soc.*, **150**, C426 (2003).
- B. Veilleux, A.-M. Lafront, and E. Ghali, *Can. Metall. Q.*, **141**, 47 (2002).
- Z. Nagy, J. P. Blaudeau, N. C. Hung, L. A. Curtiss, and D. J. Zurawski, *J. Electrochem. Soc.*, **142**, L87 (1995).
- D. N. Upadhyay and V. Yegnaraman, *Mater. Chem. Phys.*, **62**, 247 (2000).
- M. H. Holzle, C. W. Apse, T. Will, and D. M. Kolb, *J. Electrochem. Soc.*, **142**, 3741 (1995).
- G. Fabricius and G. Sundholm, *J. Appl. Electrochem.*, **15**, 797 (1985).
- T. Pearson and J. K. Dennis, *J. Appl. Electrochem.*, **20**, 196 (1990).
- D. M. Soares, S. Wasle, K. G. Weil, and K. Doblhofer, *J. Electroanal. Chem.*, **532**, 353 (2002).
- D. Stoichev and C. Tsvetanov, *J. Appl. Electrochem.*, **26**, 741 (1996).
- J. D. Reid and A. P. David, *Plat. Surf. Finish.*, **74**, 66 (1987).