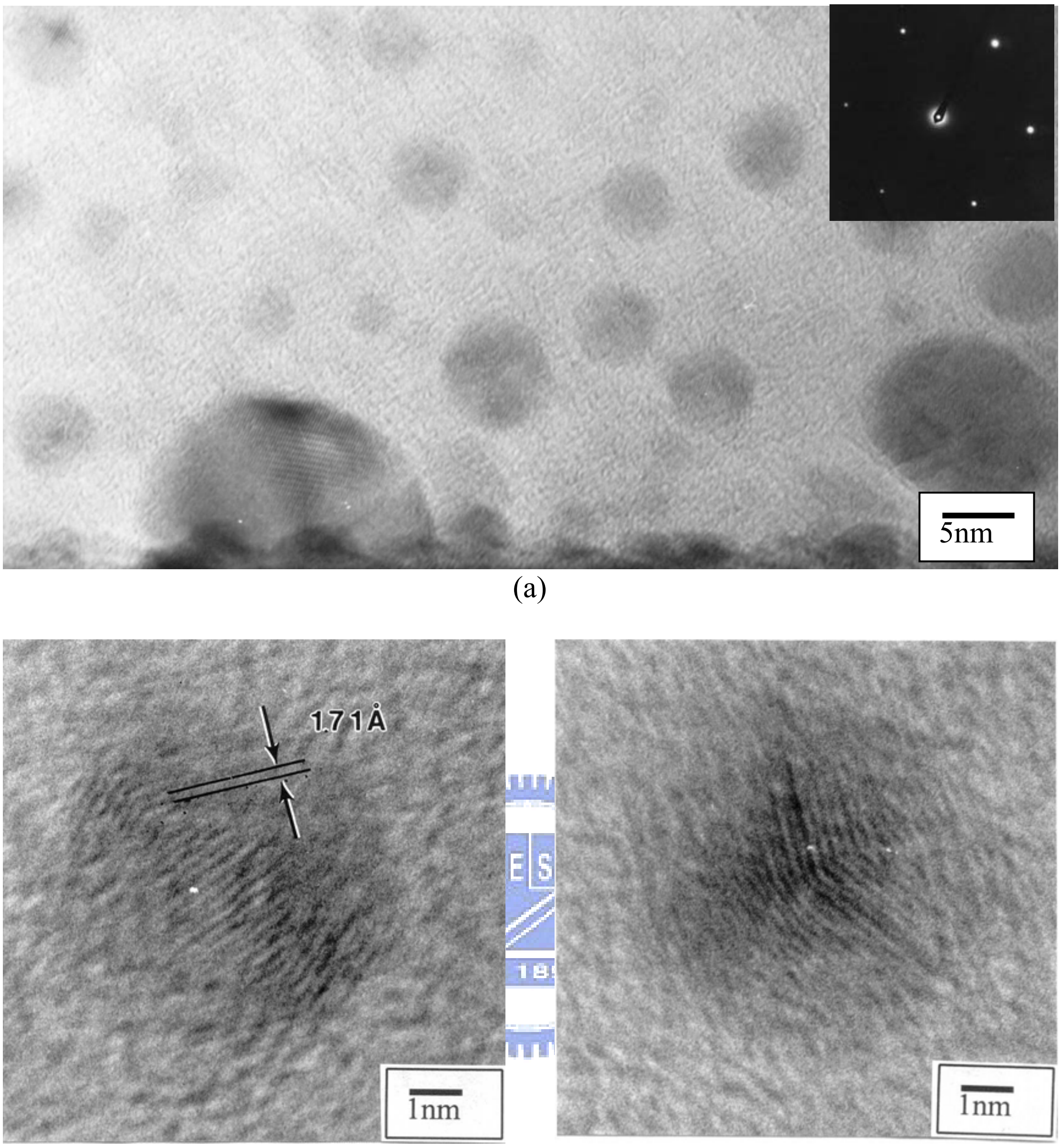


(a)

(b)

(c)

Fig. 4-11. (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 different angle.

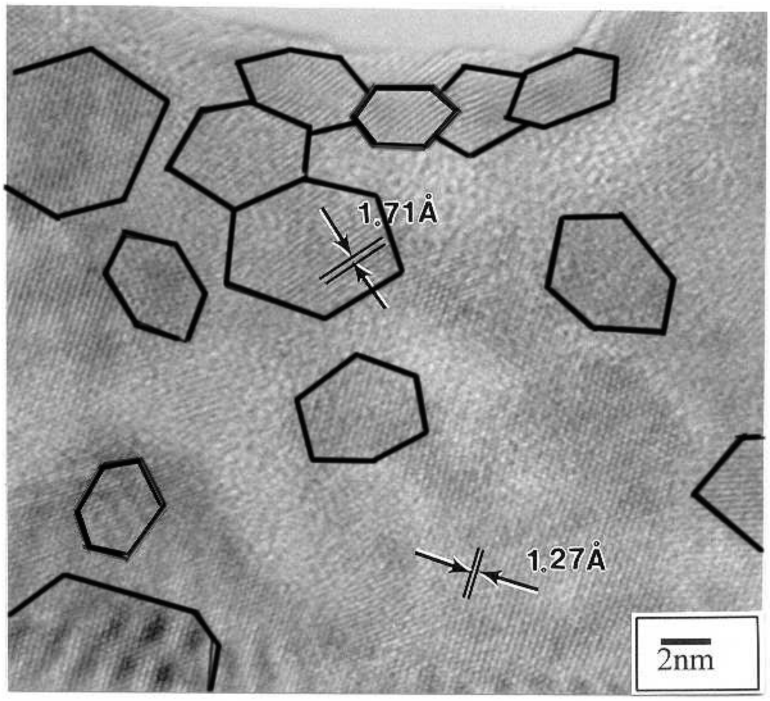


Fig. 4-12. HRTEM image showing outline of hexagonal CuCl enclosed within copper deposit formed in the presence of 360 ppm Cl^-. The plane in the image is located 5 microns from the Ti substrate surface.

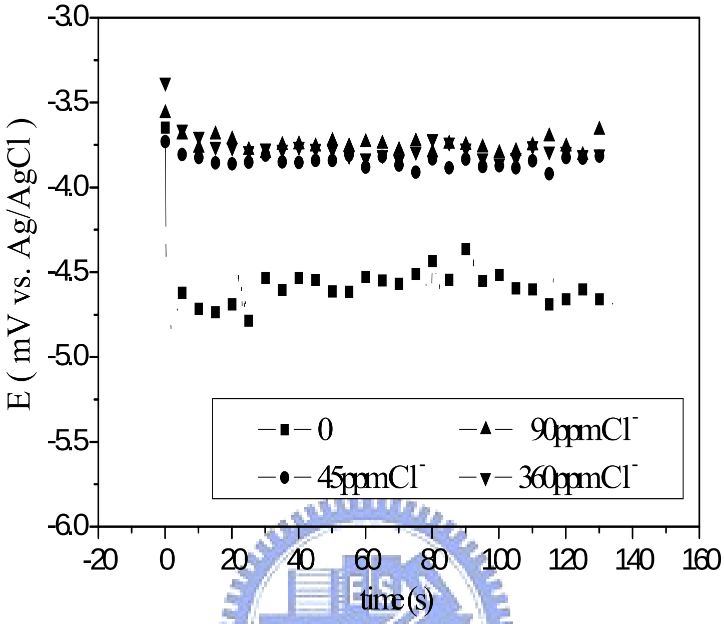
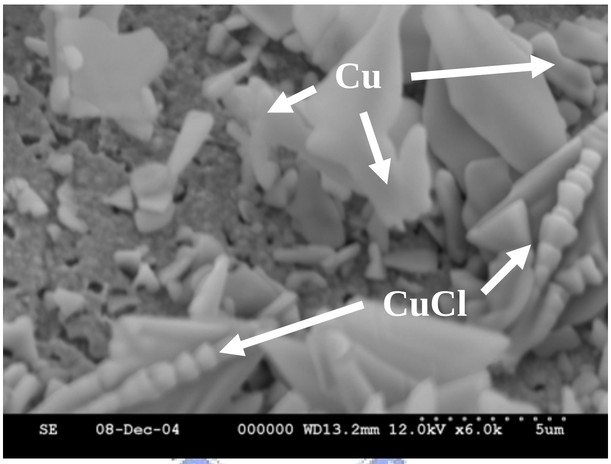


Fig. 4-13. Cathodic potential monitored during copper electroplating at 65°C on a copper substrate in sulphuric acid solution containing different Cl^- concentrations.

(a)



(b)

Fig. 4-14. 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.

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Chapter 5 Conclusions and Future Work

5.1 Conclusions

In this dissertation, two subjects were presented. First, the annealing behavior of the copper deposit, which was electroplated in the copper sulfate-sulfuric acid bath with different contents of thiourea, was discussed. In the second subject, the effect of chloride ion on the electrocrystallization of copper deposit in the copper sulfate-sulfuric acid bath with different concentrations of chloride ion was investigated. Conclusions of the above work were drawn as follows:

1. The annealing behavior of electroplated copper deposits is reported in the chapter 3. The copper deposits were electroplated with a current density of 0.7A/cm^2 in a sulfuric acid bath containing various concentrations of thiourea. An improvement of the softening resistance of the copper deposits was observed when the bath contained thiourea ≥3ppm. By adding thiourea in the plating bath, smaller grain size of the copper deposits can be achieved. As thiourea content increased ≥3ppm, the twin boundary of the copper deposits was significantly increased, and many sulfur-rich particles were deposited along the grain boundaries and a few within the grains of the deposit. These sulfur-rich particles are capable of impeding migration of the grain boundaries, and, hence, improving the softening resistance of the copper deposits during annealing.

2. The chapter 4 is to study the electrocrystallization behavior of the copper deposit on pure titanium substrate. The objective 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/cm^2 in cupric sulfate-sulfuric acid bath with various chloride additions. Results of cathodic polarization and galvanic plating experiments show that increasing concentration of chloride ion in the plating bath would significantly increase the cathodic overpotential. This overpotential 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 electrocrystallization process. At initial plating stage, copper and hexagonal-shaped CuCl precipitate was produced simultaneously. Eventually 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 Ti-substrate was further confirmed and clarified. Through overpotential and FESEM investigations, it was found that, under same electroplating condition, much less CuCl would precipitate in the much higher chloride content bath at the initial plating stage on Cu-substrate, resulting in large extent decrease of overpotential comparing with that obtained on Ti-substrate.

5.2 Future work

According to above-mentioned conclusions, there are some interesting issues work future studying regarding the property of copper deposit electroplated at high current density and high temperature condition, and they are listed as follows:

1. The efficiency of high current density with the addition of additives has been discussed in this thesis. However, in practice, pulsed current plating with additive-free solution can improve the properties of copper deposit over those achieved by DC plating. Therefore, the influence of pulse plating and additives on copper deposits electroplated from high temperature plating bath is worth studying in the future work.

2. In chapter 4, we reported that the nature of the substrate has a significant effect on the formation of CuCl, and the nature of the substrate should have an effect on the cathode potential after prolonged plating. However, the polarization and depolarization of substrate are not fully understood. Consequently, a further detail study is required to analyze the effect of the substrate, and the work is in progress.

3. Some further, advanced surface analyses are suggested to investigate the nucleation and crystallization mechanisms for copper deposition with chloride additive; this future work is expected to provide new information about CuCl formation and salt film.

4. Both electrocrystallization and deposit morphology are strongly sensitive to the presence of thiourea or chloride ions in the plating bath

at low concentrations. However, the synergetic effect of two additives on copper is not investigated in this thesis. Thus, the crystallization behavior and surface morphology of copper deposit, with both thiourea and chloride ions presented in the plating bath, is worth studying in the future work.

Publication List

Journal paper:

1. Y. L. Kao, G. C. Tu, C. A. Huang* and J. H. Chang, "The annealing behavior of the copper deposit electroplated in sulfuric acid bath with various concentrations of thiourea", **Materials Science and Engineering A,** 382, 1-2 (2004) pp. 104-111. (SCI：1.445).

2. Y. L. Kao, G. C. Tu, C. A. Huang*, T. T. Liu, " A Study on the Hardness variation of alpha- and beta-pure titanium with different grain sizes", **Materials Science and Engineering A**, 398, 1-2 (2005) pp. 93-98. (SCI：1.445).

3. Y. L. Kao, G. C. Tu and C. A. Huang*, "The Electrochemical Behavior of As-plated and 180 ^{o}C-Annealed Nano-thick Zinc-Electroplated Coppers in Aqueous Solutions with Different pH-Values", **Corrosion Science**, (2005) accepted. (SCI：1.714).

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1. C. A. Huang, S. J. Chen, G. C. Tu and Y. L. Kao, “A. C. impedance measurement in transpassive potential region of austenitic stainless steel with different degree of sensitization” , Annual Convention of Chinese Society For Material Science Engineering, 32 (2000) pp. 1-7.

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