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博士論文

添加劑對電鍍銅影響之電化學及微結構研究

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Electrochemical and Microstructural Studies of the Additives' Effects on Copper Electrodeposition

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中文摘要

這篇論文主要針對電鍍過程中添加劑對電鍍銅影響之電化學及顯微結構研究。探討電鍍過程中添加硫脲對電鍍沈積銅退火行為之影響，以及硫酸鍍液內添加不同氯離子濃度，其對於電解沈積銅之結晶行為。實驗使用硫酸銅鍍液中添加不同濃度硫脲，在高溫高電流密度下進行電鍍，利用微硬度量測電鍍沈積銅退火前後硬度的變化，並以 DSC 量測並記錄沈積銅退火時吸、放熱行為，研究沈積銅抵抗退火軟化的能力。結果顯示鍍液中含硫脲濃度高於 3ppm 時，沈積銅抵抗退火軟化阻抗能力明顯得到改善。添加硫脲於電鍍液中，可使沈積銅的晶粒尺寸細化，並且當增加硫脲含量高於 3ppm 時，沈積銅的雙晶結構明顯增加，並且可發現許多含硫顆粒沿晶界共沈積，少數含硫顆粒存在於沈積晶粒內。這些含硫量高的顆粒阻礙晶界移動，因此提高沈積銅退火的軟化抵抗能力。上述沈積銅的顯微結構以穿透式電子顯微鏡（TEM）觀察，並以 X-ray 能譜分析儀（EDS）來分析其化學組成。

在鍍液中添加不同氯離子濃度之沈積銅結晶行為，利用場射掃瞄式電子顯鏡(FESEM)及高解析穿透式電子顯鏡(HRTEM)附加成分分析，觀察分析電解沈積銅初始生長形貌及顯微結構。由陰極極化及定電流電鍍結果顯示，可知電鍍銅時陰極電位隨氯離子濃度提高而增加。由 SEM 觀察顯示在電鍍結晶過程，由於三角形氯化亞銅沈積物除了存在陰極的表面，而且形成在沈積群集銅上，造成陰極電位增加。在初始生長期間，顯示群集生長的銅和六角形的氯化亞銅沈積物同時被還原，最後可發現由許多平行之六角形面，以螺旋差排生長形成之金字塔形狀的氯化亞銅沈積物。氯化亞銅沈積物吸附上鈦陰極表

面，造成極化影響更進一步證實並且驗證，透過陰極電位量測和 FESEM 研究沈積形貌，觀察在相同電鍍條件下，銅陰極表面比鈦陰極，吸附更少氯化亞銅沈積物，導致極化影響下降。

English abstract

In this thesis, electrochemical and microstructure effects on copper electrodeposition with two additives, thiourea and chloride ion, were studied and reported. The copper electroplating was performed at relatively high temperature and high current density, which was conducted in a conventional copper sulfate-sulfuric acid bath with various concentrations of additives. The annealing behavior of electroplated copper deposits is reported in this study. Moreover, this thesis is also to study the electrocrystallization behavior of the copper deposit on pure titanium substrate.

The copper deposits were electroplated with a current density of 0.7 A/cm^2 in a sulfuric acid bath containing various concentrations of thiourea. The hardness values of the copper deposits were measured before and after annealing, and the DSC diagrams of the as-electroplated copper deposits were recorded. An improvement of the softening resistance of the copper deposits was observed when the bath contained thiourea ≥3 ppm. By adding thiourea in the plating bath, smaller grain size of the copper deposits can be achieved. As thiourea content increased ≥3 ppm, 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. The aforementioned microstructures of the copper deposits were examined with transmission electron microscope (TEM) integrated with energy-dispersive x-ray spectrometer (EDS) for chemical composition analysis.

The electroplating was conducted at 0.7 A/cm^2 in cupric sulfate-sulfuric acid bath with various chloride additions. Initial growth morphology and microstructure of the deposit were examined with field-emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM) integrated with energy dispersive X-ray spectrometer (EDS). Results of cathodic polarization and galvanostatic plating experiments show that the increasing concentration of chloride ion 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 electrocrystallization process. At initial plating stage both copper and hexagonal-shaped CuCl precipitate 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 the 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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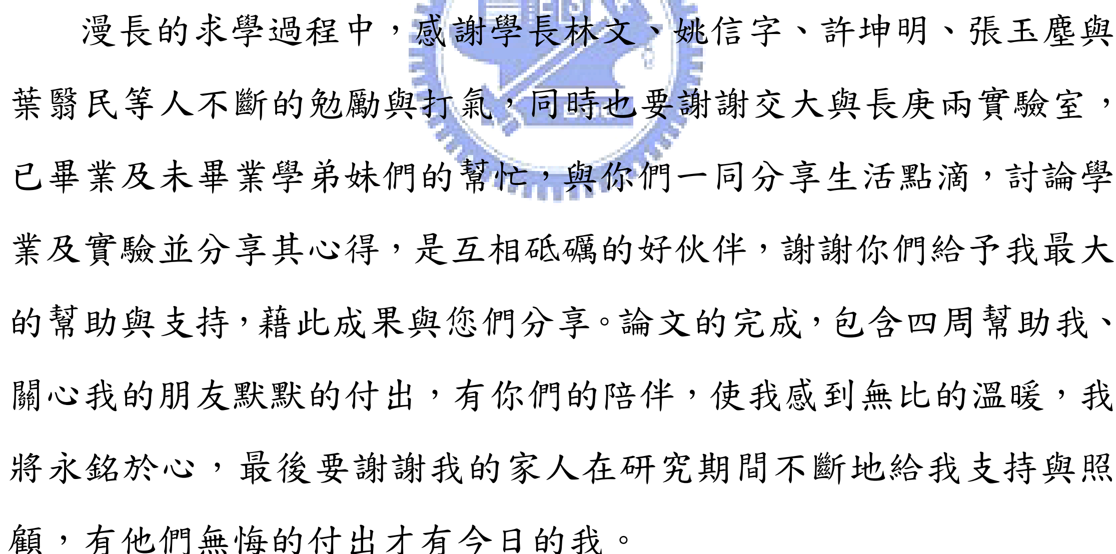

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Chapter 1 Introduction

1.1 Background

Electroplated copper deposit is widely used in the electrical industry due to its low electrical resistance and high thermal conductivity [1-3]. In addition, copper deposit has suitable mechanical, chemical and physical properties [4-6]. Thus, the electroplated copper deposit is the potential material for advanced interconnect materials of printed circuit board (PCB) and integrated circuit (IC) products [7, 8].

Over the past several decades, electrochemical deposition of copper has been performed in various methods, such as electroplating [9-10], electroforming [11-13], electrorefining [14-16] and electrowinning [17-19]. Among these methods, copper electrodeposition is the commonly used method for producing advanced interconnects materials. It gives a number of advantages including high yield, rapid processing and relatively low cost [20, 21]. Technology for copper electrodeposition was developed in 1930, and applied for roof leakage protection. In 1950, the copper deposit was used in the electronic industry, and met tremendous demands of electronic commodities. Recently, various features of copper deposits were employed in the conducting materials of printed circuit board in which high circuit density and superior properties of conducting element in the printed circuit is required [22, 23]. Therefore, improving the properties of the copper deposit is an important issue nowadays.

In industrial application, thiourea and chloride ion are the most commonly used additives in copper electrodeposition [24-27]. The

purposes of the additives were to control the surface morphology, microstructure and mechanical property of copper deposit. Numerous studies have been done to find the role of thiourea and chloride ion for copper electrodeposition [28-29]. However, in spite of extensive study, there are still many unknown aspects concerning the effect of additives on eletrocrystallization of copper deposit. Besides, many studies have focused on the behavior of the copper electrodeposition and deposit at low temperature and low plating current density [30-31]. Little is known the effect of thiourea or chloride ion on the copper electrodeposition at high current density and high temperature, at which high deposition rate for copper deposit could be achieved. In this dissertation, the annealing behavior of the copper deposit, which was electroplated in the copper sulfate-sulfuric acid bath with different contents of thiourea, was discussed. 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.

1.2 Motivation

It is well known that the copper deposit is widely used as electrical conducting material in various electronic devices [32-34]. Recently, high physical, chemical and mechanical properties of the copper deposit are required because relatively small and compact electronic devices are in great demand [35, 36]. In order to improve the properties of copper deposit, additives are used during copper electroplating. The additives, chloride ion and thiourea, are commonly used for improving the microstructure, morphology, and characteristics of copper deposits [37-39].

The property of copper deposit can be significantly improved by adding small amount (~ppm) of thiourea in the plating bath [40-42]. Numerous publications have given details about the influence of thiourea additive on the appearance and properties of the copper deposit [24, 25, 43], contributing to the understanding of the electrocrystallization mechanism [44, 45]. However, little is known that the annealing behavior of copper deposit was electroplated in the copper bath with various contents of thiuorea. In this dissertation, the annealing behavior of copper deposits was characterized with microhardness measurement and DSC analysis. The results were fully discussed with the microstructures of copper deposits.

It is well known that adding chloride ion in sulfuric acid bath for copper electroplating is required to improve the surface brightness and mechanical properties of the deposit [35, 46]. It has been reported that the addition of small amount of chloride ions (~10 ppm) in acidified copper plating bath would accelerate the reduction reaction of cupric to cupreous ion. On the other hand, formation of cupreous chloride [47, 48] or even

an insoluble salt film [26, 49] 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 cupreous chloride and/or the salt film formations. The electrocrystallization of copper deposit electroplated in the copper bath with different concentrations of chloride ion was investigated by using field emission scanning microscope (FESEM) and high-resolution transmission electron microscope (HRTEM).

1.3 Overview of this study

In this thesis, chapter 1 describes the aplication of copper deposit and presents two articles related to copper electrodeposition. In addition, the motivation of this dissertation is also described. Chapter 2 is literature review, briefly illustrating the electrocrystallization mechanism of copper deposit and the effect of chloride ion and thiourea on copper electrodeposition. Chapter 3 describes the annealing behavior of copper deposit electroplated in the plating bath with various concentrations of thiourea. In this chapter, the microstructures of as-plated and annealed copper deposits were analyzed with transmission electron microscope and compared with the results of microhardness measurement and DSC analyses. In Chapter 4, the effects of chloride ion on the electrocrystallization of copper deposit and on the cathodic potential variation of copper electroplating were discussed. The aim of this chapter is to investigate the crystallographic structure of cupreous chloride on the titanium and copper cathode surfaces. We concluded that the effect of chloride ions on the cathodic polarization of copper electrodeposition depends strongly on what kinds of cathode materials were used. Finally, the conclusions of this dissertation and the recommended further work are stated in chapter 5.

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Chapter 2 Literature Review

2.1 Metal electrodeposition

The electrodeposition of metal deposit requires the passage of current between two electrodes that are immersed in an electrolyte with metallic ions. The electrodeposition reaction is accompanied by the transfer of electrons from an external electron source to the electron gas in the metal. A soluble anode acts as an electron sink for oxidation reaction and provides enough metallic ions for electrodeposition on the cathode surface. Thus, the anode has the same composition as the reduced deposit which is desired for electrodeposition on the cathode surface. As shown in Eq. 2-1, metallic ions transfer from the anode crystal lattice into the electroplating bath during electrodeposition, meanwhile some metal ions in the bath adjacent to the cathode are reduced on the cathode surface (presented in Eq. 2-2) [1, 2].

$$M_{lattice} \xrightarrow{anode} M^{+z}{}_{electroplating-bath} + ze^{-} \quad \ldots\ldots\ldots\ldots(2-1)$$

$$M^{+z}{}_{electroplating-bath} + ze^{-} \xrightarrow{calalytic-surface} M_{lattice} \quad \ldots\ldots(2-2)$$

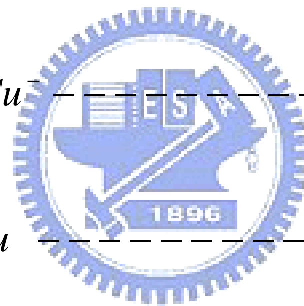
Where z is the number of electrons involved in the reaction. The amount of metal deposit on the cathode surface follows the Faraday's law, which states that the amount of electroplated metal is proportional to the amount of electroplating charge.

In this study, copper electrodeposition was performed in an electrochemical three-electrode configuration. The working electrode for electrodeposition was made from pure titanium (99.5 wt%, ASTM Grade

2), which was fabricated in a cylinder form with an exposed area of 1.0 cm^2 (8.4 mm in diameter and 4 mm in length). A platinized Ti-mesh was used as counter electrode. An $Ag/AgCl_{sat.}$ was used as the reference electrode. Owing to superior corrosion resistance in the copper plating electrolyte, the pure titanium electrode was widely used as the cathode for copper electroplating [3-5].

In the reduction process of cupric ions, cupric ions must first diffuse from bulk solution to the cathode surface and reduce from metal ion into adsorption metal atom. It is accepted by several researchers that the reduction of cupric ion follows two-step reactions in the copper acid bath [6-8]:

$$Cu^{2+} + e^{-} \rightarrow Cu^{+} \text{ ------------- } (2-3)$$



$$Cu^{+} + e^{-} \rightarrow Cu \text{ ------------- } (2-4)$$

The two-step reduction of cupric ion is generally accepted as the basic reaction for copper deposition. Bockris [9, 10] found that the rate is limited by the charge transfer in the first-step (in Eq. 2-3) at high current density. At low current density the rate of deposition is controlled by surface diffusion of copper adatom. The presence of small concentrations of additive in plating baths has been reported to improve copper deposit properties by some researchers [66, 67]. During a slow growth of the copper deposit, this additive effectively suppresses the vertical growth of the copper deposit, while enhancing the lateral spreading. Richard et al. [11] studied the influence of chloride and nitrate anions on copper electrodeposition in ammonia media. The results showed a two step

reduction for the copper deposition, where the first step of Cu(II) to Cu(I) is under diffusion control and second reaction Cu(I) to Cu is influenced by the reduction of Cl^- and NO_3^- [12].

The copper deposit has been of much interest for the interconnection material of printed circuit boards (PCBs) and ultra large scale integration (ULSI). Therefore, the copper deposit by electroplating in the acidified copper bath has been studied extensively [13-16]. In this work, we investigate the copper deposit using high electroplating current density in the acidified copper bath containing different contents of throurea or chloride ion. We characterize the cathodic polarization behavior of copper electroplating in the plating baths by using the rotating cylinder electrode (RCE). The electrocrystallization of copper deposits, which were electroplated in the baths with different concentrations of chloride ion, was investigated. The annealing behavior of copper deposits, which were electroplated in the baths with various contents of thiourea, was studied. The microstructures of the copper deposits were characterized by field-emission electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM).

2.2 Effect of additives on the electrocrystallization of copper deposit

Section 2.1 describes briefly the electrocrystallization process. Namely, phase transformation from metal ions in the solution to metal atoms on the electrode surface was presented [1]. This phase transformation is a sequence process with ionic transport, discharge, surface diffusion, nucleation, and growth [17, 18]. In general, electrocrystallization process can be divided into two processes, i.e. nucleation and growth. These two processes have been intensively studied with both theoretical and experimental methods.

Nucleation is a very important process in metal deposition. The granularity of metal deposit is strongly affected by nucleation rate. The nucleation rate of metal deposit depends on the existing degree of supersaturation, which is determined by the cathodic overpotential in electrodeposition processes. The nucleation rate increased with increasing the ratio of cathodic current density and metallic ion concentration in solution, and the higher the nucleation rate the finer grain size of deposit [19-21]. The growth form is strongly affected by electroplating overpotential. Winand [22] reported the growth form of copper deposit in the acidified copper bath. With an increasing of cathodic overpotential, the growth form of copper deposit gradually changes from pyramids, to columnar crystals, to lamellae, and to polycrystalline.

Most investigation focused on the electrodeposition process and electrocrystallization behavior of copper deposit in aqueous solutions [23-25]. Several studies [26-28] reported that the electrodeposition process depends on the coupled interaction of several variables, such as (1) current density, (2) temperature, (3) additives type and (4) substrate conditions. Characterizing and monitoring the effect of these variables on

the metal electrodeposition is important to improve its physical and mechanical properties. The information concerning the effect of additives on copper electroplating has been discussed in section 2-3.

Many studies showed the effects of additives on the electrocrystallization of copper deposit [29-31]. Adsorbed additives affect the kinetics of electrodeposition and the growth mechanism by changing the concentration of growth sites on a surface [32-34]. In addition, different types of additives may be considered having different effects. The additives can change the structure of the double layer, and thus influence the charge transfer overpotential [35, 36]. Paunovic and Arndt [37] have shown that additives may have two opposing effects, acceleration and inhibition, on the reduction of Cu^{2+} ions. For example, guanine and adenine have accelerating effect on the cathodic reduction of Cu^{2+} ions in the electroless copper bath. Several studies [38-40] have proved that small amounts of chloride ion are known to have an accelerating effect on the copper electrodeposition. Muresan et al. [41] reported that the polarization effect could be considered as the nucleation inhibition due to the occurrence of specific adsorption on the copper surface. It suggests that additives or their complex adsorbed on the cathode surface and resulted in an obvious increase of cathode potential during copper electrodeposition. The increase of cathodic potential caused by adsorption of additives on the copper surface was also proposed by Fischer [42] and Nichols [43].

Although the kinetic mechanism of copper electrodeposition has been well established [25, 44-46], there are still many unknown aspects concerning the effect of additives on eletrocrystallization of copper deposit. In this study the effect of chloride ions on the initial growth of

copper deposit on the titanium and copper cathode electrodes investigates. The annealing behavior of copper deposits, which were electroplated in the acidified copper baths with a thiourea content from 1 to 10 ppm, were studied.

2.3 Effects of electroplating parameters

2.3.1 Effects of plating current density on copper electroplating

A number of studies have shown the influence of electroplating parameters on the physical and mechanical properties of copper deposit [47-49].The parameters, bath temperature, plating current density, additives and substrate materials are the most concerned issues. Several researches [26, 50-52] reported that the morphology and the microstructure of copper deposit are markedly affected by the electroplating current density. Fig. 2-1 shows a typical cathodic polarization behavior, current-potential curve, of copper electrodeposition. The potential is scanned from the equilibrium potential toward negative potential, the current increases in an exponential manner where the overall deposition rate is determined largely by charge transport at the cathode [53]. However, the current density lies in what fraction of the limiting current density is of important concerned. That is, the normalized parameter, the ratio between plating current density and limiting current density, I / I_L, is often used to characterize the property of copper deposit. Winand [54] reported that growth model of polycrystalline copper deposit in the acidified copper bath without additive (Fig. 2-2). According to the inhibition intensity and plating current density, different growth model of a metal deposit can be found. The Winand-diagram can be successfully used for copper electrodeposition in the acidified copper bath. However, the electrocrystallization behavior is still not fully studied when organic additives are added to the bath.

Several studies [55-57] have focused on the surface morphology and mechanical property of the copper electrodeposition at low plating current density in the acidified copper plating bath with various amount

of additives. Yokoi et al. [58] investigated the current-voltage behavior of copper electroplating when PEG was added in the plating bath. They proposed that copper ions were held by PEG molecules, and these PEG molecules could adsorb on the surface of copper deposit. Hence, the charge transfer resistance increased owing to the absorption of PEG molecules. Kelly and West [59, 60] found that PEG inhibits the copper electrodeposition reaction in the presence of chloride ions and the reaction was proven by using quartz crystal microbalance (QCM) and electrochemical impedance spectroscopy techniques.

Recently, copper electroplating has been applied for on-chip interconnection in microelectronics [28, 61], in which grain distribution and mechanical property of the copper deposit has attracted much attention [62-64]. Numerous publications [55, 56, 65] proposed that the growth model of copper deposit was depended on the electroplating current density. It is accepted that a nodular surface could be obtained when relatively high electroplating current density was applied. That is, the surface roughness of the copper deposit increased with an increasing electroplating current density. However, many researchers [26, 66, 67] showed that the morphology and growth model of copper deposit can be significantly affected when copper electroplating in the bath with an addition of additives. The copper deposit with leveling or even brightening surface can be achieved at high plating current density when adding additives in the plating bath. These additives act mostly as inhibitors, adsorbent on the cathode surface where they take part in the electrocrystallization of copper deposit [26, 55, 68]. Some additives also increase the deposition overpotential. However, many reports have focused on the behavior of the copper electrodeposition at low

temperature and low plating current density. Little is known about the effect of additives on the copper electrodeposition at high plating current density and high temperature. In present work copper electroplating was performed at relatively high temperature and high current density. Two subjects were studied with copper deposits. In the first subject, 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.

2.3.2 Effect of additives on copper electroplating

It is well known that additives play an important role in the copper electrodeposition process. It is well known the mechanical and physical properties of copper deposit can be significantly improved when electroplating in the bath with an addition of additives. Additives were generally studied individually by adding them in parts per million (ppm) [43, 47]. The result reported that the introduction of small amount of additives in electrodeposition baths leads to marked changes in the nature of copper deposits obtained at the cathode. That is, both electrocrystallization and deposition kinetics are strongly sensitive to small amount of additives in the plating bath. The effects of various additives, such as chloride ion [28, 49], thiourea [64, 69], gelatin [70, 71], benzotriazole (BTA) [72] and polyethylene glycol (PEG) [58, 59], on the behavior of copper deposit were studied and reported by many researchers. In general application, copper plating baths contained more than one additive. Typically, they influence deposit morphology and microstructure by adsorbing on the cathode and inhibiting reduction process during electrodeposition.

The additives used for copper electrodeposite are generally organic compounds that act as inhibitors, grain refiner, and may be co-deposited with copper. According to their function, the additives can be classified into three kinds: suppressor, leveler and accelerator.

1. Suppressor:

In general, suppressor is one type of polymers, such as PEG, that influence the charge transport property in the grain boundaries. Since it usually blocks the active sites on the surface and inhibits the deposition reaction, it is also called inhibitor. Inhibitors form a polymeric film [73,

74] or salt film [49] on the substrate surface and exhibit a barrier which impedes mass transfer of copper ions to the surface. Stoychev et al. [75] showed that the addition of PEG or PPG to acidified copper plating bath increases the overpotential of copper deposition. Other studies [66, 76] also proposed that adsorption of a low concentration of PEG is enough to block the active nucleation sites leading to an increase of copper electrodeposition overpotential.

2. Leveler

The leveler is used to decrease the surface roughness of metal deposit. The leveler has the ability to diminish surface nodular and void [37]. It acts by adsorption at crest positions on the deposit surface and inhibits the deposition rate of the positionsl. Generally, electroplating with leveler is a mass-transfer controlled process due to its low solubility in the plating bath and low coefficient of diffusion. In industrial electrodeposition application, gelatin and thiourea are widely used as leveler to control surface morphology and leveling agent of copper deposit [47, 48, 70].

3. Accelerator/ Brightener

The brightener is a molecule that contains sulfur and may also incorporate other functional groups. Brightener is commonly used to reduce microscopic roughness (< 1 μm) of the deposit. Compared to the wavelength of the incident light, the surface roughness is so smaller that the light is reflected rather than scattered [77]. It is accepted that the brightener acts by a modification of the nucleation process and, therefore, change the Tafel slope. These additives promoted a shift of deposition potential to more negative values during copper deposition. The copper

reduction process was then hindered to some extent [37].

In practice, some additives may act simultaneously as leveling and brightening, such as thiourea, chloride ion and gelatin. The leveling and brightening generally consist of small organic molecules and/or salts containing sulfur and/or nitrogen that interact with the cathode surface. Literature review of additives, thiourea and chloride ion, was presented as follows;

- **Thiourea**

Thiourea is commonly used as a brightening agent during copper deposition through adsorption on the cathode surface [78-82]. Suaraz et al. [26] reported that the significant leveling effect for copper deposit was found when small amount of thiourea (~ppm) was added in the cupric sulfate-sulfuric acid bath. Several studies [31, 80-82] reported that the thiourea inhibits deposition by blocking active sites on the surface through adsorption. The initial increase in inhibition efficiency is suggested to be due to increasing the coverage on cathodic surface by a monolayer of thiourea molecular. In other words, thiourea forms a bond on the copper surface via its unsaturated sulfur atom, thereby inhibiting the surface diffusion of the copper adatoms and promoting a smaller-grained structure [59, 83-85]. Fleischmann et al. [86] employed SERS to examine the adsorption of thiourea on silver and copper electrodes in K_2SO_4 as well as HCl solution. The result suggested that only a single thiourea molecule is involved in complex formation with a copper adatom at the electrode surface.

In principle, thiourea influences the charge transfer during deposition process, either via S^{2-} generation, followed by CuS precipitation [87], or by forming adsorbed $[Cu(Tu)_n]^+$ (n=1, 2, 3, 4) complex species, which block the active electrode sites and deliver copper slowly by dissociation [88, 89]. Alodan et al. [81] showed that thiourea forms stable complexes with both cupric and cuprous ions in the solution, and the complexes adsorbed on the cathode surface. Thus the adsorbed species inhibit surface diffusion of partially reduced adions [36, 90].

The growth form of copper deposit is strongly affected by the concentration of thiourea contained in the electroplating bath. Alodan et al. [63] investigated the growth behavior of copper deposit with cofocal laser scanning microscopy (CLSM), by which the initial growth morphology of the deposit profile could be examined in micrometers. The techniques of atomic force microscope (AFM) and the scanning tunneling microscope (STM) have been used to investigate the early stage of the electrocrystallization [91]. The grown of copper deposit exhibit formation of three-dimensional islands atop initially flat plates, reflecting a two-stage growth mechanism. A number of studies have shown the influence of thiourea on the mechanical property of the copper deposit [8, 26, 55], contributing to the understanding of the electrocrystallization mechanism [41, 92]. These studies presented that the adsorption of thiourea on the cathodic surface inhibited copper deposition and changed the electrocrystallization property of the copper deposit. However, in spite of this extensive study, there are still many unknown aspects concerning the copper deposition mechanism when thiourea was added in the plating bath.

In the chapter 3 of this study, the annealing behavior of electroplated copper deposits electroplated in the sulfuric acid bath with various concentrations of thiourea is reported. Specifically, the softening resistance microstructure of the annealed copper deposit is introduced in the chapter 3. Although we anticipate that though conclusive evidence can be obtained mainly by transmission electron microscope TEM, but we have strong evidence that smaller grain size, more sulfur-rich deposits and larger twin boundaries are qualitatively rationized to be responsible for the good softening resistance exhibited after annealing.

- **Chloride ion**

Addition of chloride ion in copper plating bath is known to control the surface morphology and refine the grain size of copper deposits [39, 93-95]. Small amounts of chloride ion in the acidified copper plating bath accelerate the reduction reaction from cupric to cupreous ion. This supports the hypothesis that chloride ions act as binding sites for surfactant. Whereas, at high concentration (>0.1 M) [96], chloride ions were found to increase copper electrodissolution in acidic solution with the formation of cuprous chloride complex [97, 98] or even unsolutable salt film [36, 49] on the cathodic surface, leading to impeding the deposition process. Thus, increasing chloride ions in the plating bath, the cathodic potential of copper deposition becomes more negative.

Chloride ion is known to form insoluble CuCl and soluble $CuCl^{-}_{2}$ species in solution, which have the capacity to affect the deposition process [38, 99-101]. Several studies have investigated the influence of chloride ion in the copper plating bath [49, 102]. Peykova et al. [103] reported that the effect of chloride ion is due to potential

dependent adsorption on the electrode surface and on the growing clusters on the substrates. Copper deposition on copper disk in acid-sulfate plating solution containing chloride ions, organic additives and hydrodynamics was studied by Yoon with the rotating ring-disk electrode (RRDE) [36]. It is suggested that in addition to CuCl surface films, adsorbed Cu(I) or Cu(I) complex Cl bridge films inhibit surface diffusion of adsorbed Cu atoms, and this becomes the rate determining step in the deposition mechanism.

Several studies have found that the presence of chloride ion tends to decrease the overpotential for Cu^{2+} reduction on copper substrate during galvanostatic plating. Kelly et al. [59] found that small amount of chloride ions could be used as surface activator for accelerating the reduction of copper ions and achieving a depolarization effect. Goldbach et al. [97] also confirmed its depolarizing effect and the negligible hindrance of CuCl film to charge-transfer. The enhancements in the rate of Cu^{2+} reduction due to chloride ion were reported in the related researches [39, 104].These studies were in good agreement and demonstrated that the Cu^{++}/Cu^{+} reaction is strongly catalyzed by trace amounts of chloride ions in the solution. The Cu^{++}/Cu^{+} reaction was found to be unaffected by chloride ions. Nagy et al. [39] has been attributed to the formation of a bridge between Cu^{2+} and Cl^{-} with a shorter spacing than that of Cu^{2+}/H_2O/metal bridges in chloride-free systems. However, other studies that have reported the opposite finding the presence of chloride ion tend to polarization Cu^{2+} reduction. The polarization effect of chloride ions on copper deposition was proposed by several literatures [3, 47, 105]. The authors show that the CuCl precipitate has a stronger tendency to form on the Ti substrate than deposited copper.

Despite numerous studies on the influence of thiourea and/or chloride ion on the electrodeposition process, little is known regarding the form in which they adsorb on the cathodic surface. The aim of the present work was to study the adsorption of chloride ion, utilizing cupric sulfate-sulfuric acid bath with various chloride additions (45-350 ppm). This study of the chapter was carried out using the measurement techniques of cathodic polarization and galvanostatic plating. Initial growth morphology and microstructure of the deposit were examined with FESEM and HRTEM integrated with EDS.

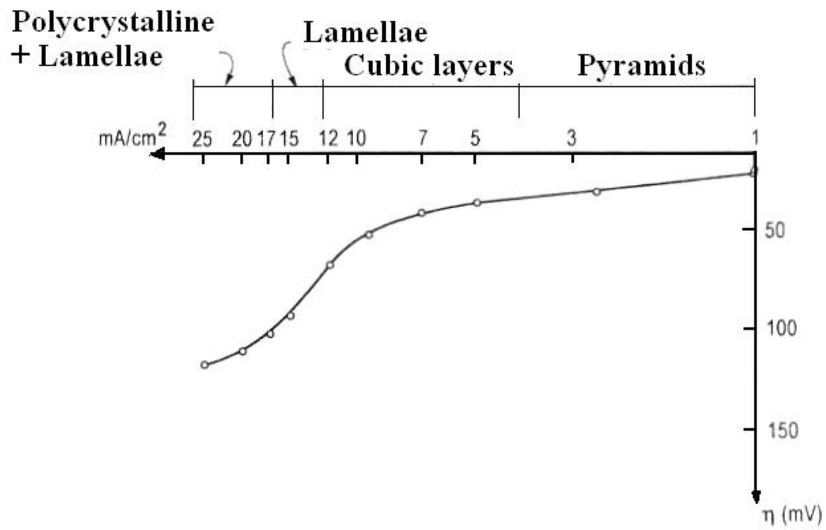


Fig. 2-1 Overpotential characteristic of transition from compact to powdery deposit in electrodeposition of copper from copper sulfate-sulfuric acid bath [53].

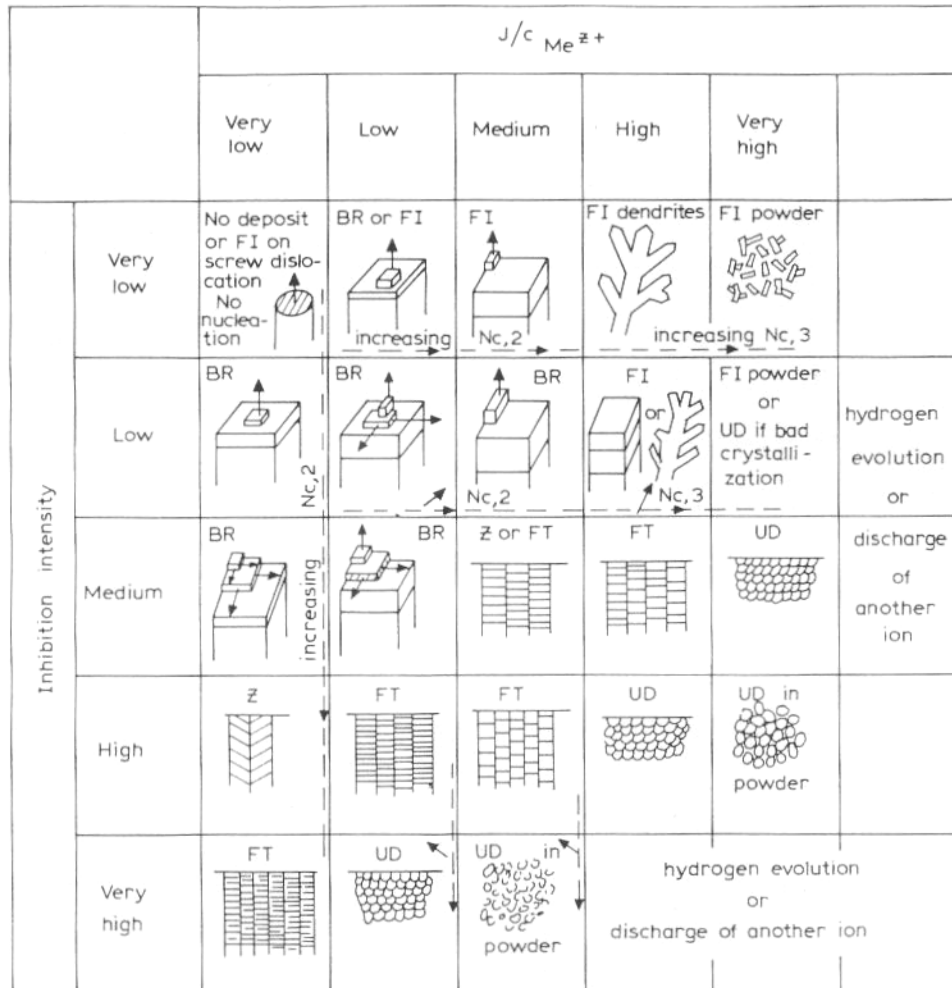


Fig. 2-2 Detailed schematic diagram showing different possible type of polycrystalline electrodeposits as a function current density and inhibition intensity [54].

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Chapter 3 The annealing behavior of copper deposit electroplated in sulfuric acid bath with various concentrations of thiourea

3-1 Introduction

Owing to its low electrical resistance, high thermal conductivity and economical cost, the copper deposit is widely used as the electrical conducting material in the electronic devices, such as print-circuit board (PCB) and IC products. In recent years, high physical, chemical and mechanical properties of the copper deposit are required because smaller compact electronic devices are in great demand [1, 2]. Therefore, improving the properties of the copper deposit is an important issue nowadays. It is well known that the properties of copper deposit can be significantly improved by adding small amount (~ppm) of thiourea in the plating bath [3-5]. Numerous publications have given details about the influence of thiourea additive on the appearance and properties of the copper deposit [6-9], contributing to the understanding of the electrocrystallization mechanism [10,11].

It is recognized that recovery and recrystallization of a metallic specimen may occur when the specimen is subjected to annealing at high temperatures. Without moving of the grain boundaries, some zero- and one-dimensional crystalline defects, vacancies and dislocations, can be partly annihilated in the recovery process [12]. However, softening microstructures [13], such as formation of subgrain with very low dislocation densities and grain growth, were developed during recrystallization in which migration of grain boundaries occurs through

the driving force of dislocation density (primary recrystallization) or the difference of the grain size (secondary recrystallization) [14]. In the study of the annealing behavior of the electroplated copper, Surmev et al. [15] found that recovery and recrystallization could proceed in the eletrodeposited copper when the deposit was exposed to room temperature for 30 days. Abrahams et al. [16] studied the annealing behavior of copper deposits electroplated in the bath with leveling agent. They found that many tiny Cl^- and S^- rich particles being deposited in the copper matrix and impeding the movement of the boundary dislocations. Although adding thiourea in the copper-electroplating bath is commonly utilized, the effect of thiourea added in the plating bath on the annealing behavior and the related microstructures of electroplated copper have not get been fully investigated.

In this paper, the annealing behavior of electroplated copper deposits using a thiourea/sulfuric acid bath is reported. Hardness measurement and DSC analysis of the copper deposits were performed to explore the softening resistance of the deposits during annealing. Metallographic examination of the deposits using optical microscope (OM) and transmission electron microscope (TEM) were conducted to study the behavior of the softening resistance of the annealed copper deposit.

3.2 Experimental Procedure

A rotating cylinder electrode (RCE), which was fabricated from pure titanium (99.5 wt%, Grade 2) in cylinder form with an exposing area of 1.0 cm^2 (8.4 mm in diameter and 4 mm in length), was used as the cathode in all electroplating experiments. The copper electroplating was performed in a conventional copper sulfate-sulfuric acid bath composed of $CuSO_4 \cdot 5\ H_2O$ (90 g/L), H_2SO_4 (120 g/L) with thiourea addition in a range from 1ppm to 10ppm. The copper electroplating was conducted at constant current density of 0.7 A/cm^2, 53±0.5^{o}C for 135 seconds to obtain a copper deposit with a thickness ca. 35μm. The experiment flowchart is shown in Fig. 3-1.

The rotation speed of the RCE, in the rotating disc-cell kit EG&G RDE 0001, was kept constant at 2000 rpm. The three-electrode type electrochemical plating cell was constructed. A platinized Ti-mesh and $Ag/AgCl_{(sat.)}$ were used as counter and reference electrodes, respectively. The RCE was used as the working electrode. The cathodic Ti-surface of the RCE was mechanically ground to 1200 grit finish using emery paper, cleaned in acetone, dried with cold air blaster and then prepared for copper electroplating. After electroplating, the copper deposit was carefully peeled off the Ti-cathode, acoustically cleaned in acetone, and then dried for further study. In order to investigate the annealing behavior of the copper deposit, a differential scanning calorimetry (DSC; TA instruments Inc. DSC 2010) was utilized, with scanning temperatures range from 30°C to 400°C and scanning rate of 10°C /min. For each DSC-analysis, ca. 6mg sample of as-electroplated copper deposit was required and prepared. To study the softening resistance of the copper deposit, the hardness of both as-electroplated and annealed deposits was measured. Annealing of the copper deposit was

carried out at 350°C for 30 minutes in air. The hardness of the copper deposit was tested with 10g load of the diamond-indenter equipped in Matsuzawa Digital Microhardness Tester (Model MXT-α7e). The mean hardness with its standard deviation was calculated through five measurements made in the middle of the cross section of the deposit in arbitrary positions. To avoid the effect of self-annealing on the copper deposit at room temperature [14], all measurements and investigation of the copper deposits were carried out within one day after electroplating.

The metallographic cross section of the copper deposit was examined with optical microscope. Sample with a dimension of 15 mm x 5 mm was taken, mounted in epoxy, milled by sand paper, polished by diamond paste, and immersed in the etchant, consisting of 98% NH_4OH + 2% H_2O_2, for 5 seconds before optical examination of the microstructure. The microstructure of the copper deposit was also studied with transmission electron microscope (TEM, Jeol 2000FX) integrated with energy-dispersive X-ray spectrometer (EDS, Links ICIC), which allowing for local chemical composition analysis. The TEM-samples were prepared using a twin-jet electrochemical cell (Fischion Instruments, Inc.). The jet-polishing was carried out in the 40% H_3PO_4 electrolyte at 5.0 V until a tiny hole being produced in the middle of the specimen, around which the sample was so thin that made TEM/EDS examination and analyzing feasible. The grain size of copper-deposit was statistically evaluated by line intersection method, by which four TEM-micrographs at 50,000 magnifications were taken on arbitrary middle positions of the deposit parallel to its plating surface. A set of parallel lines with equal distance of 1 cm was then drawn on these four micrographs. The grain size of the deposit was calculated based on the sum of intersected points

of the line and grain boundary from each of the drawn lines, and was defined as the length of total drawn lines divided by total intersecting points.

3.3 Results and Discussion

3.3.1 Hardness of the copper deposits

Fig. 3-2 represents the effect of thiourea concentration on the hardness of as-electroplated and annealed copper deposits. The result illustrates that the hardness of as-electroplated copper deposit increased with increasing thiourea content (0-8 ppm) prior to a slight decrease of the hardness with thiourea content from 8 ppm to 10 ppm. On the other hand, the hardness of as-electroplated coppers annealed at 350°C for 30 minutes were greatly decreased to ca. 2.87 GPa (85Hv) for deposits electroplated in lower contents of thiourea ($\leq$ 1.0 ppm). The hardness of the annealed copper deposits, electroplating in the bath containing thiourea $\geq$3 ppm, could be maintained to the level of at least 3.87GPa (124 Hv). Hence, it indicates that increasing thiourea content in the plating bath tends to increase the hardness of as-electroplated copper and, also, increase the softening resistance during annealing of the deposit. However, for full understanding of the annealing behavior, the copper deposits must be further characterized with DSC-analysis and microstructures examination using specially TEM analysis.

3.3.2 DSC-analysis

The results of DSC-analysis of the copper deposits between 30~400°C are shown Fig. 3-3. It can be clearly seen that the exothermic peak temperatures of the copper deposits were affected by the content of thiourea added in the plating bath; the higher contents of thiourea the higher exothermic peak temperatures. The exothermic peak temperature of DSC-analysis is closely related with softening property of the copper deposit, i.e. higher softening resistance of copper deposit occurs with presence of higher exothermic peak temperature in DSC-analysis, as

illustrated in the following sections. Comparing the result of hardness variation shown in Fig. 3-2 with the exothermic peak temperatures of Fig. 3-3, it is apparent that adding thiourea in the plating bath, both the hardness and softening resistance of the as-plated copper can be increased.

From the results of hardness measurement and DSC analysis of the deposits, two interesting facts are worth notifying. First, the softening resistance of the copper deposit could be increased when the deposit was electroplated with bath thiourea content ≥3 ppm. Second, slight decrease in the hardness of the copper deposit and the slightly lower exothermic peak temperature of the copper deposit were detected when the deposit was electroplated with bath thiourea content changing from 5 ppm to 8 ppm. To rationalize the two facts, it is required that the annealed microstructures of the copper deposit be further studied with optical microscope and transmission electron microscope.

3.3.3 Microstructural examination

3.3.3.1 Optical microscopy

Fig. 3-4 shows the cross-section microstructures of the copper deposits electroplated with different bath content of thiourea. For deposits without and with 1 ppm thiourea, tilted columnar structure comprised most of the cross-section micrograph. On the contrary, perpendicular (to Ti substrate) columnar structure prevailed in the deposits with thiourea content ≥5 ppm. Increasing the thiourea concentration (≥5 ppm), a surface leveling effect of the deposit could be observed, this complies with the results of Suarez [17] and Maher [8], which reported that leveling and brightening of the copper deposit surface could be achieved

when electroplating copper in acidified sulfate bath with thiourea addition. The grains of the copper deposit were not so clearly resolved that the grain size could not be directly evaluated with optical microscope.

The cross-section micrographs of the copper deposits annealed at 350°C for 30 minutes are shown in Fig. 3-5. Typical abnormal grain growth occurred in the copper deposits during annealing. Many fine equiaxed grains with many larger speckle grains were the structure features present in Figs. 3-5c and 3-5d, which specimens were electroplated with bath thiourea content ≥3 ppm. In contrast, larger equiaxed grains were developed in the copper deposits electroplated in lower (≤1 ppm) and nil thiourea-content baths after annealing (Fig. 3-5a and 3-5b). Therefore, from the metallographic examination, it seems that the difference in the softening resistance of the annealed copper deposits could be ascribed to the difference in grain size as well as its distribution; the smaller grain with narrower size distribution the higher hardness.

3.3.3.2 TEM examination

Typical TEM-micrographs of as-electroplated copper deposits plated in the bath with different thiourea contents are shown in Fig. 3-6. The relationship between grain size of copper deposits and bath thiourea content is shown in Fig. 3-7. With addition of 1 ppm thiourea, the grain size of the copper deposit was increased from 162 nm, that of the deposit with no addition, to 169 nm. Furthermore, the grain size decreases from 169 nm to 152 nm with increasing bath thiourea content from 1 ppm to 8 ppm. In the micrographs of as-electroplated copper deposits, the slight amount of twin boundary could be observed in the copper deposit with 1 ppm thiourea addition (Fig. 3-6b); however, very large amount twin boundary was found on the deposits electroplated in the bath with higher

thiourea content (≥3 ppm) (Figs. 3-6c~3-6e). The formation of these twins play role an strengthening to certain extent because twin boundaries, with different planar orientation, can act as obstacles to dislocation motion and thus tend to increase the hardness. Some authors already indicated that the twin boundaries are strong obstacles to restrain dislocation over slip boundaries [18, 19]. Thus, it can be reasonably recognized that the main strengthening factor for the as-electroplated copper deposits plated specimens is the amount of grain boundary area in the specimens; therefore, the smaller grain size, the higher hardness. However, it is difficult to quantify this effect since estimation of twin boundary area is a no-easy work, not mention that the great extent of orientation variation between comprising grains would make the quantification infeasible.

Scrutinizing the micrographs (Fig. 3-6), many tiny spherical particles, arrow-indicated, were found in the copper deposit as thiourea-content increased to ≥3 ppm (Figs. 3-6c~3-6e). From the result of typical EDS-analysis shown in Fig. 3-6f, it demonstrates that the particle was merely composed of copper and sulfur, which was resulted from the presentation of thiourea in the plating bath. The size of the particle increases with increasing thiourea content in the plating bath. Furthermore, the sulfur-rich particles deposit preferably along the grain boundaries (Figs. 3-6d~e). Direct evaluation from the TEM micrographs displays that there is little obvious structure with high dislocation density in the deposits shown in Fig. 3-6. Consequently, it is reasonable to say that the driving force for primary recrystallization in subsequent annealing at 350°C relates very little to the dislocation density.

Comparing Fig. 3-2 with Fig. 3-7, it shows that higher added

thiourea concentration, which causing decreasing grain size, would result in hardness increase of the as-electroplated copper deposit. However, effects of other features, like twin boundary and sulfur-rich particle, on the hardness still need further investigation.

The TEM-micrographs of the annealed copper deposits electroplated with different thiourea contents were shown in Fig. 3-8. It can be seen that the grain growth occurred in all deposits during annealing at 350°C, e.g. the grain size increase from 169 nm to 350 nm after annealing for the deposit plated in the bath with 1 ppm thiourea. The sulfur-rich particles (as identified by the EDS-analysis of the typical arrow-indicated particle in Fig. 3-8 and shown in Fig. 3-8f) in the annealed copper deposits grew simultaneously with increasing thiourea content in the bath. It is interesting to notice that the particle density in the deposit increased in the case with thiourea-content $\geq$8 ppm. The abnormal grain growth occurred in the middle and outer parts of annealed deposits (Fig. 3-5). The sulfur-rich particles in the copper deposit would certainly play an important role in the migration of the grain boundaries during annealing. When grain boundaries move across these particles, the dragging force exerted by these particles on the moving grain boundaries acts and, hence, impeding grain growth. From the TEM-micrograph shown in Fig. 3-9, migration of the grain boundary across sulfur rich particles can be observed in the annealed copper deposits. This is quite different from the particles in the as-plated copper deposits, in which most of the sulfur-rich particles are found locating along the grain boundaries (Figs. 3-6d~e).

The above ratiocination is proved by the fact that the softening resistance of the copper deposit increased as thiourea content increasing

to ≥3 ppm. From the TEM-micrographs shown in Figs. 3-6 and 3-8, many tiny particles in the copper deposit could be observed, when adding thiourea to ≥3 ppm. Hence, the softening resistance of the annealed copper deposit was raised to a great part obviously by adding thiourea content to ≥3 ppm.

It is well known [12, 13, 20] that high density of small particles in the metallic substrate can effectively impede the movement of the grain boundaries during annealing. It seems that the slightly lower sulfur-rich particle density with larger particle size in the copper deposits with bath thiourea content of 8 ppm (Fig. 3-8e) causes the slight decrease for both of the exothermic peak temperature and the hardness. However, the softening resistance of the annealed copper deposits, with bath thiourea content ≥8 ppm, was still much higher than those of the annealed copper deposits with bath thiourea content ≤1 ppm. In the annealing process, grain growth is inevitable, which would result in the decrease of hardness to certain extent; and the many sulfur-rich particles observed in Figs. 3-6c~3-6e obviously contributes to mitigate the drawback and bring forth the good softening resistance.

3.4 Summary

The effects of annealing on the hardness and the microstructure for copper deposits electroplated with varying thiourea were investigated. The hardness of as-electroplated copper deposits increased with increasing thiourea content, but that of annealed copper deposits decreased only a small extent with bath thiourea content ≥ 3ppm, exhibiting good softening resistance.

In the TEM micrographs of as-electroplated copper deposits, it was estimated that the grain size decreases with increasing bath thiourea content. Many sulfur-rich particles were found co-deposited with copper and precipitated mostly along the grain boundaries for the copper deposit electroplated in the bath thiourea content ≥3 ppm. Great amount of twin boundary was observed in the copper deposit electroplated with and without thiourea addition. Those features i.e. smaller grain size, more sulfur-rich deposits and larger twin boundaries are qualitatively rationized to be responsible for the good softening resistance exhibited after annealing.