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

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Abstract

The annealing behavior of electroplated copper deposits is reported in this study. The copper deposits were electroplated with a current density of 0.7 A/cm^2 at 53 °C 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 differential scanning calorimetry (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 mg/L. By adding thiourea in the plating bath, smaller grain size of the copper deposits can be achieved. As thiourea content increased ≥ 3 mg/L, 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 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 (EDX) for chemical composition analysis.

Keywords: Annealing; Copper deposit; Thiourea; Softening resistance; Sulfur-rich particle deposit

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 (∼mg/L) 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 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, Surnev and Tomov [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 impede the movement of the boundary dislocations. Although adding thiourea in the copper-electroplating bath is commonly utilized, the effect of thiourea added in

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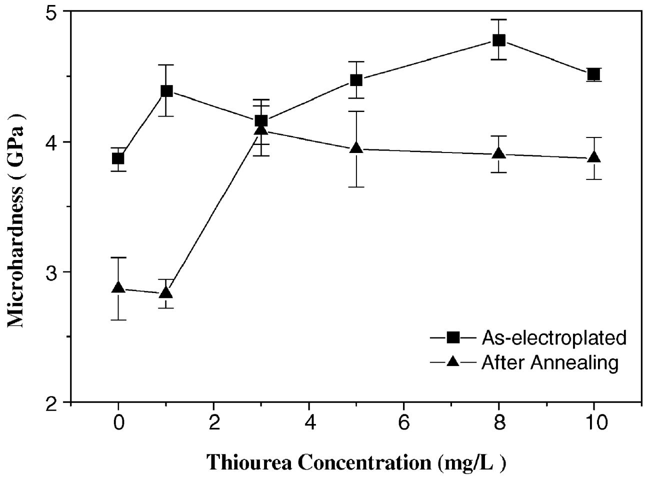

Fig. 1. The hardness variation of the copper deposits after 350 °C annealing for 30 min and in relation with various contents of thiourea in the plating bath.

the plating bath on the annealing behavior and the related microstructures of electroplated copper have not been fully investigated.

In this paper, the annealing behavior of electroplated copper deposits using a thiourea/sulfuric acid bath is reported. Hardness measurement and differential scanning calorimetry (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.

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 $CuSO_4 \cdot 5H_2O$ (90 g/L), H_2SO_4 (120 g/L) with thiourea addition in a range from 1 to 10 mg/L. The copper electroplating was conducted at constant current density of 0.7 A/cm^2, 53 ± 0.5 °C for 135 s to obtain a copper deposit with a thickness approximately 35 μm.

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 from 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 (TA Instruments Inc. DSC 2010) was utilized, with scanning temperatures range from 30 to 400 °C and scanning rate of 10 °C/min. For each DSC analysis, approximately 6 mg 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 cop-

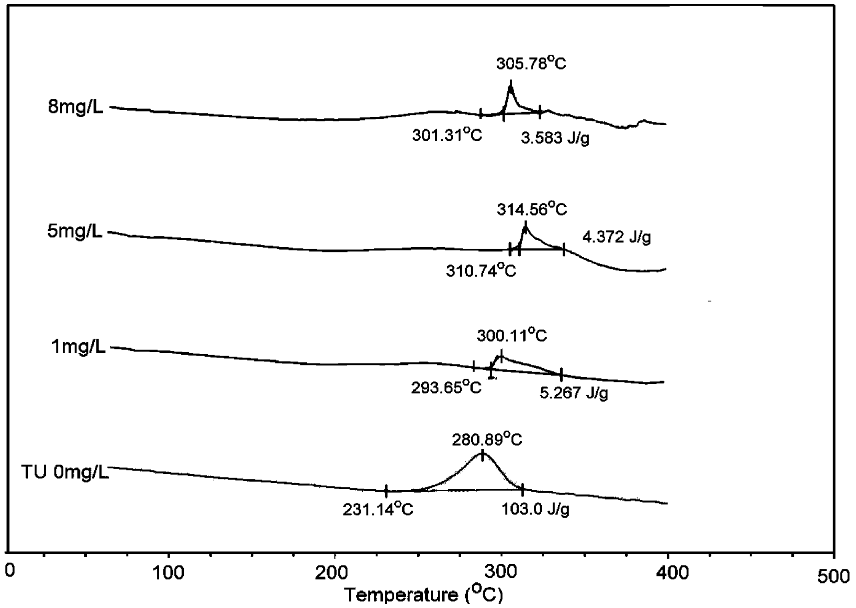

Fig. 2. The results of DSC scanning of the copper deposits electroplated in various contents of thiourea (scanning rate: 10 °C/min; scanning temperature range 30–400 °C).

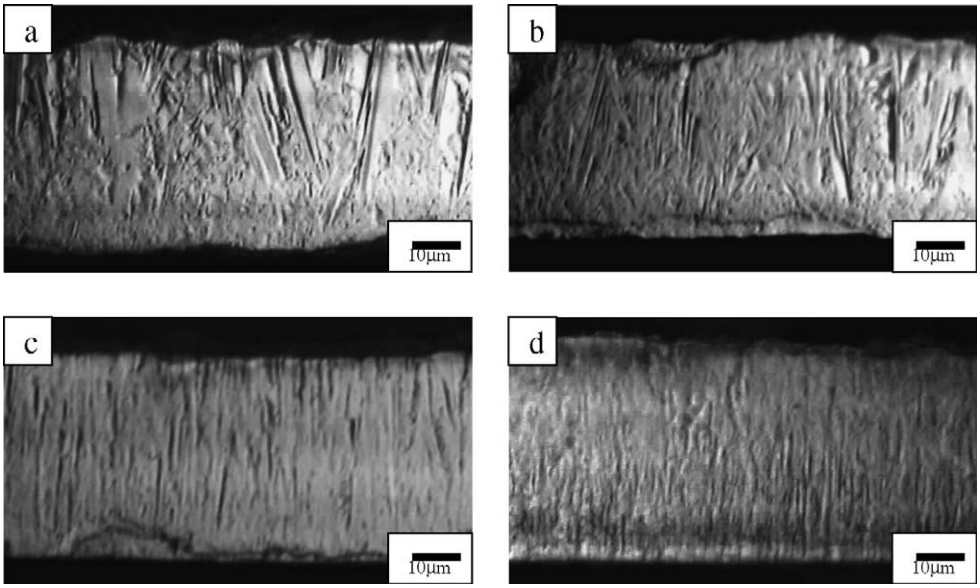

Fig. 3. Cross-section micrographs of the as-electroplated copper deposits plated in the bath with various concentrations of thiourea: (a) 0 mg/L, (b) 1 mg/L, (c) 5 mg/L, and (d) 8 mg/L (etched specimen, optical microscope).

per deposit was carried out at 350 °C for 30 min. The hardness of the copper deposit was tested with 10 g 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 1 day after electroplating.

The metallographic cross section of the copper deposit was examined with optical microscope. Sample with a dimension of 15 mm × 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 s before optical examination of the microstructure. The microstructure of the copper deposit was also studied with transmission electron microscope (Jeol 2000FX) integrated with energy-dispersive X-ray spectrometer (EDX, Links ICIC), which allows for local chemical composi-

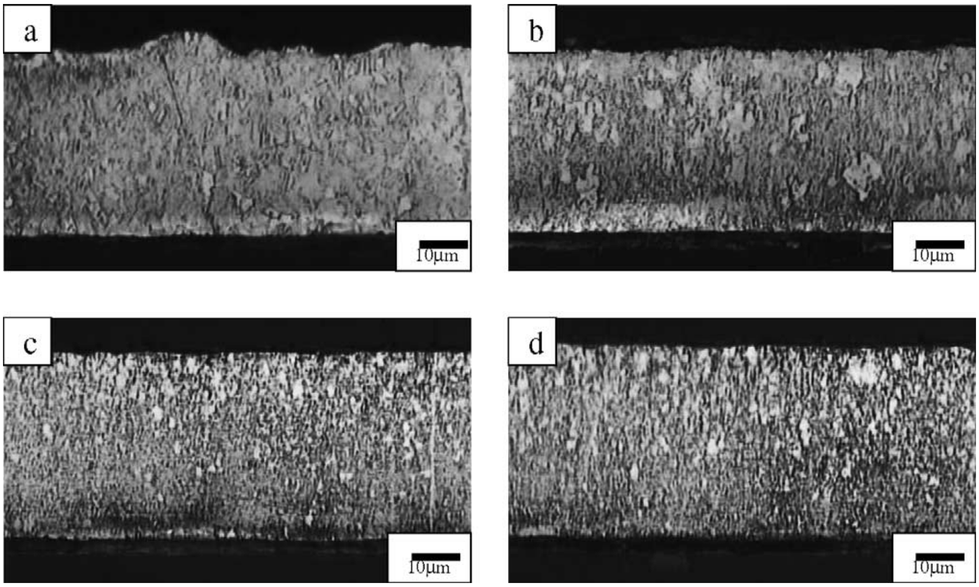

Fig. 4. Cross-section micrographs of the annealed copper deposits plated in the bath with various concentrations of thiourea: (a) 0 mg/L, (b) 1 mg/L, (c) 5 mg/L, and (d) 8 mg/L (etched specimen, optical microscope).

tion 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 V until a tiny hole being produced in the middle of the specimen, around which the sample was so thin that made TEM/EDX examination and analyzing feasible. The grain size of copper-deposit was statistically evaluated by line intersection method, by which four TEM micrographs

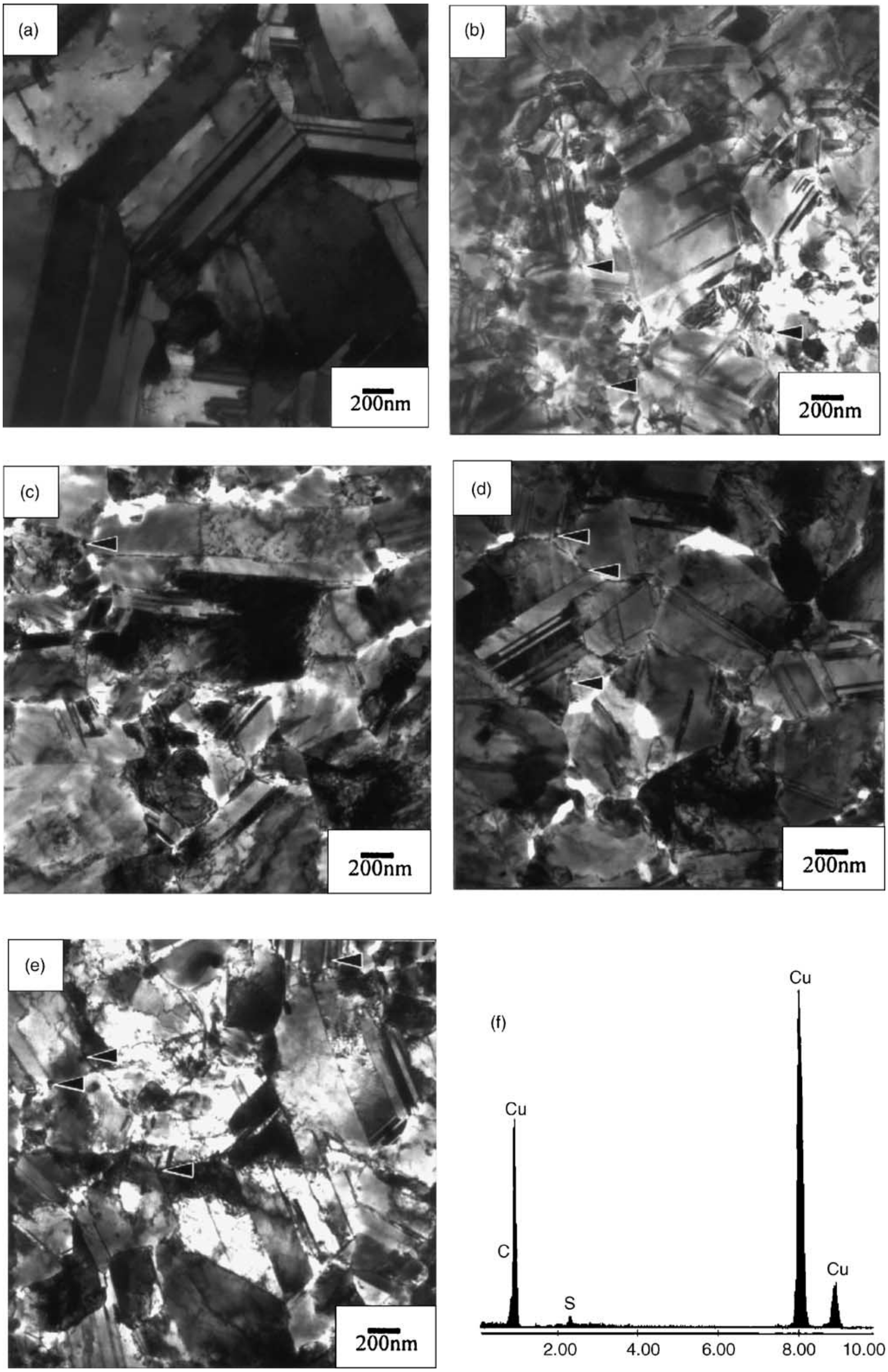

Fig. 5. TEM micrographs of the as-electroplated copper deposits plated in the bath with various concentrations of thiourea: (a) 0 mg/L, (b) 1 mg/L, (c) 3 mg/L, (d) 5 mg/L, (e) 8 mg/L, and (f) EDX analysis on the particles indicated by arrows.

at 50,000 magnification 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. Results and discussion

3.1. Hardness of the copper deposits

Fig. 1 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 mg/L) prior to a slight decrease of the hardness with thiourea content from 8 to 10 mg/L. On the other hand, the hardness of as-electroplated coppers annealed at 350 °C for 30 min were greatly decreased to approximately 2.87 GPa (85 Hv) for deposits electroplated in lower contents of thiourea (≤1.0 mg/L). The hardness of the annealed copper deposits, electroplating in the bath containing thiourea ≥3 mg/L, could be maintained to the level of at least 3.87 GPa (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.

3.2. DSC analysis

The results of DSC analysis of the copper deposits between 30 and 400 °C are shown in Fig. 2. 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 the 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. 1 with the exothermic peak temperatures of Fig. 2, 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 mg/L. 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 to 8 mg/L. 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. Microstructural examination

3.3.1. Optical microscopy

Fig. 3 shows the cross-section microstructures of the copper deposits electroplated with different bath content of thiourea. For deposits without and with 1 mg/L 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 mg/L. Increasing the thiourea concentration (≥5 mg/L), a surface leveling effect of the deposit could be observed, this complies with the results of Suarez and Olson [17] and Alodan and Smyrl [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 min are shown in Fig. 4. 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 Fig. 4c and d, which specimens were electroplated with bath thiourea content ≥3 mg/L. In contrast, larger equiaxed grains were developed in the copper deposits electroplated in lower (≤1.0 mg/L) and nil thiourea-content baths after annealing

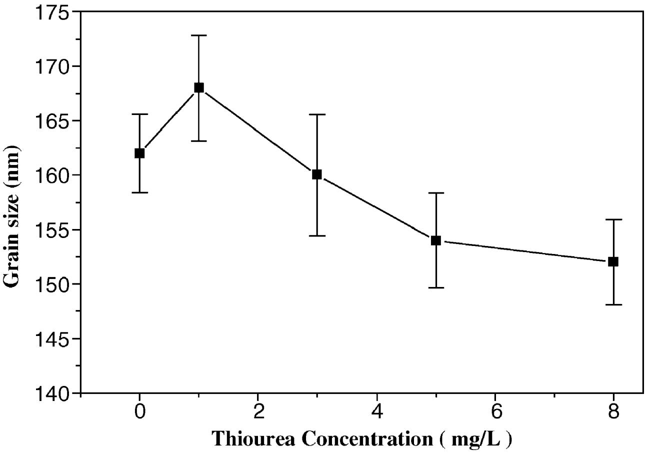

Fig. 6. Results of grain size measurement versus the as-electroplated copper deposits plated in the bath with various concentrations of thiourea.

(Fig. 4a and b). 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 the grain with narrower size distribution, the higher the hardness.

3.4. TEM examination

Typical TEM micrographs of as-electroplated copper deposits plated in the bath with different thiourea contents are shown in Fig. 5. The relationship between grain size of copper deposits and bath thiourea content is shown in Fig. 6.

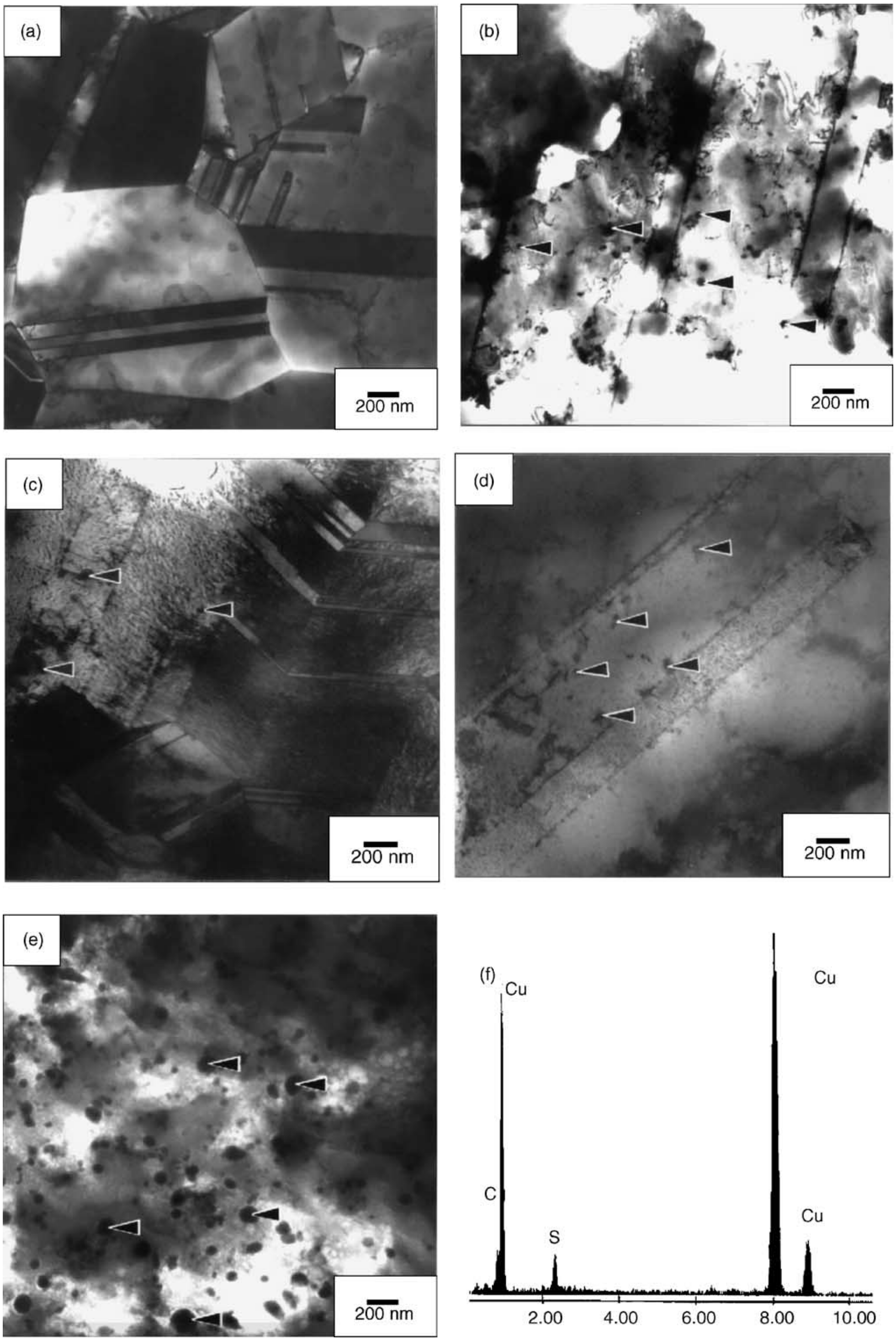

Fig. 7. TEM micrographs of the annealed copper deposits plated in the bath with various concentrations of thiourea: (a) 0 mg/L, (b) 1 mg/L, (c) 3 mg/L, (d) 5 mg/L, (e) 8 mg/L, and (f) EDX analysis on the particles indicated by arrows.

With addition of 1 mg/L 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 to 152 nm with increasing bath thiourea content from 1 to 8 mg/L. In the micrographs of as-electroplated copper deposits, the slight amount of twin boundary could be observed in the copper deposit with 1 mg/L thiourea addition (Fig. 5b); however, very large amount twin boundary was found on the deposits electroplated in the bath with higher thiourea content (≥3 mg/L) (Fig. 5c–e). The formation of these twins plays a role in strengthening to a 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]. 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. 5), many tiny spherical particles, arrow-indicated, were found in the copper deposit as thiourea-content increased to ≥3 mg/L (Fig. 5c–e). From the result of typical EDX analysis shown in Fig. 5f, 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 (Fig. 5d–e). Direct evaluation from the TEM micrographs displays that there is little obvious structure with high dislocation density in the deposits shown in Fig. 5. 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. 1 with Fig. 6, 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. 7. It can be seen that the grain growth occurred in all deposits during annealing at 350 °C, e.g. the grain size increases from 169 to 350 nm after annealing for the deposit plated in the bath with 1 mg/L thiourea. The sulfur-rich particles (as identified by the EDX analysis of the typical arrow-indicated particle in Fig. 7 and shown in Fig. 7f) 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 ≥8 mg/L. The abnormal grain growth occurred in the middle and outer parts of annealed deposits (Fig. 4). 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. 8, 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 (Fig. 5d–e).

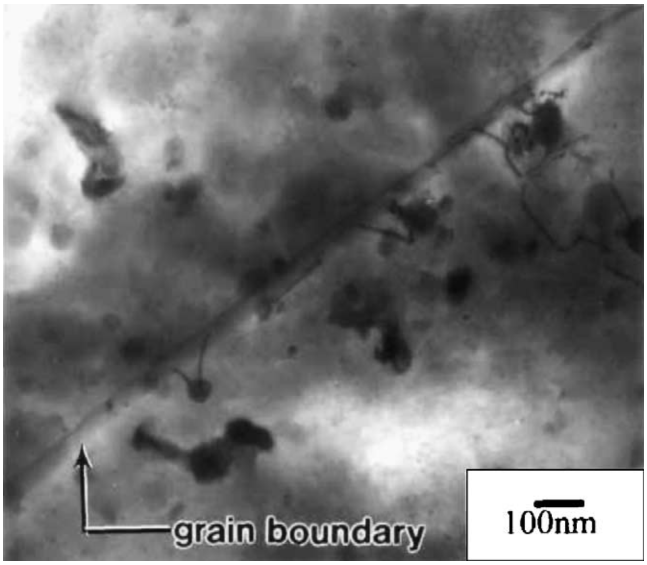

Fig. 8. TEM micrograph showing migration of the grain boundary across sulfur-rich particles in the annealed copper deposit plated with 5 mg/L thiourea.

The above ratiocination is proved by the fact that the softening resistance of the copper deposit increased as thiourea content increasing to 3 mg/L. From the TEM micrographs shown in Figs. 5 and 7, many tiny particles in the copper deposit could be observed, when adding thiourea to ≥3 mg/L. Hence, the softening resistance of the annealed copper deposit was raised to a great part obviously by adding thiourea content to ≥3 mg/L.

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 mg/L (Fig. 7e) 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 mg/L, was still much higher than those of the annealed copper deposits with bath thiourea content ≤1 mg/L. 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 Fig. 5c–e obviously contribute to mitigate the drawback and bring forth the good softening resistance.

4. Conclusion

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 ≥3 mg/L, 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 mg/L. 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.

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