



Electropolishing behaviour and microstructures of copper deposits electroplated in an acidic copper-sulphuric bath with different thiourea contents



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ABSTRACT

Cu electrodeposition was performed on a rotating cylindrical Ti electrode in Cu-sulphate plating baths with different thiourea contents up to 8 ppm. The hardness, microstructure and electropolishing behaviour of the Cu deposits were studied. Some sulphur-rich particles in the Cu deposits prepared from the thiourea-containing baths were identified. The sulphur-rich particles dissolved preferentially during electropolishing in a 40 vol.% H₃PO₄ solution, forming a thin amorphous phase containing P in patches on the outer surface of the Cu deposit. The deposits prepared in the baths with thiourea showed higher dissolution current during polishing and formed a brightened and levelled surface with a surface roughness (R_a) lower than 30 nm.

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1. Introduction

The physical properties of Cu deposits, such as hardness, strength, and toughness, are improved by adding a few ppm of thiourea to the Cu plating bath [1–3]. Thiourea is commonly used as a brightening or levelling agent for Cu electroplating. It functions by interacting strongly with the surface of the cathode and inhibiting the diffusion of the adsorbed Cu atoms on the cathode surface, producing a smooth and bright electroplated surface [4]. The thinning process of the Cu deposit has recently attracted significant attention for applications in the field of industrial technology, such as Cu-foil electroforming, printed-circuit-board and semiconductor technologies; however, there remains a lack of reports on the electropolishing behaviour of Cu deposits prepared in a thiourea-containing Cu-plating bath.

Many researchers [5–7] have reported that metal substrates are electropolished in an electrolyte when a limiting-current plateau is detected in the anodic polarisation curve. Regardless of the presence of different grain orientations, crystal defects, and even phases, the surface of the metal substrate can be levelled and brightened during electropolishing [8–10]. Many researchers [11,12] have demonstrated that a Cu substrate can be electropolished well in aqueous phosphoric acid solutions. Electropolishing is a diffusion-controlled process driven

by selective electrochemical dissolution that depends on the concentration gradient of the diffusing species [13,14]. Electropolishing typically occurs at the high anodic potential located in a limiting current plateau in which the metal surface becomes brightened and smoothed. Some defects and pitting are formed on the surface by the evolution of oxygen gas at a potential higher than the limiting-current plateau [15].

In this work, the effect of adding of thiourea to the Cu plating bath on the microstructures and hardness of the Cu deposits, and the electropolishing behaviour of the Cu deposits in a 40 vol.% H₃PO₄ solution were investigated. The correlation between the microstructures and the electropolishing behaviour of the Cu deposits was discussed.

2. Experimental procedure

Cu electroplating was conducted in plating baths containing 365 gL⁻¹ CuSO₄·5H₂O, 120 gL⁻¹ H₂SO₄ and 0, 1, 3, 5 or 8 ppm thiourea. The main chemical compositions were widely used for fabrication of Cu foils [16,17]. The electroplating was conducted in an electrochemical three-electrode cell. The rotating cylinder electrode (RCE), or the working electrode, was made of pure Ti (grade 2), and it had a diameter of 8.4 mm and a length of 4 mm. A platinised Ti-cylinder mesh and an Ag/AgCl electrode in a saturated KCl solution were used as the counter and reference electrodes, respectively. In this study, all of the potential values for the electroplating and electropolishing tests in whole text refer to the Ag/AgCl reference electrode in a saturated KCl solution (0.199 V vs. SHE). The Ti-RCE was mechanically polished with 2000 mesh emery paper, washed in distilled water, rinsed in ethanol, and dried with air blaster. The electroplating experiments were conducted

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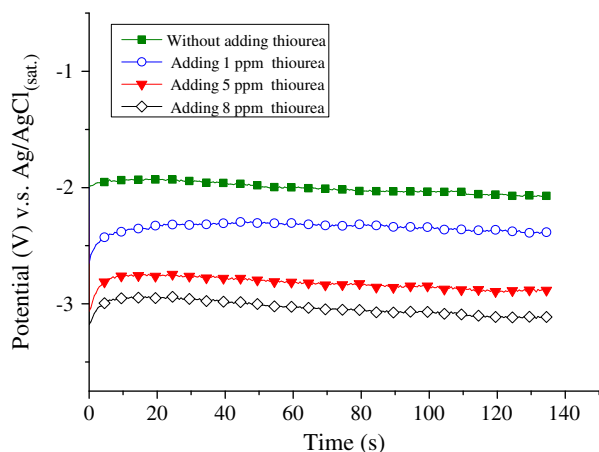


Fig. 1. Variation of cathodic overpotential during electroplating at 70 Adm^{-2} in the Cu-sulphate plating bath.

at $50 \pm 1 \text{ }^\circ\text{C}$ in a circulated water bath. The Cu electroplating was performed with a constant current density of 0.7 Acm^{-2} for 135 s to obtain a Cu deposit with a thickness of ca. $35 \text{ }\mu\text{m}$.

The microstructures of the Cu deposits were examined with a transmission electron microscope (TEM, Jeol 2000FX). The TEM samples were prepared with a twin-jet electrochemical cell (Fischion Instruments, Inc.) in an aqueous 40% H_3PO_4 solution at 70 V and room temperature. The specimen was jet-polished until a tiny hole was produced in its middle side, around which the TEM/EDX examination and analysis were feasible. The TEM specimens were also prepared with ion-milling to avoid the reaction of the Cu deposit with 40% H_3PO_4 solution during twin-jet etching. In this process, the Cu deposits were mechanically dimpled to a thickness of $5 \text{ }\mu\text{m}$ and then bombarded with an Ar^+ ion beam at an accelerating voltage of 5 kV to achieve a thin area for electron-beam imaging and diffraction.

The hardness of the Cu deposit was measured using a Digital Microhardness Tester (Matsuzawa, MXT- $\alpha 7e$) with a load of 10 g. Before hardness measurement, the Cu deposits were mounted vertically to reveal their cross sections. The mounted cross-sectional Cu deposits were polished with diamond paste to a mirror finish. The mean hardness and its standard deviation of a Cu deposit were evaluated according to five measurements conducted approximately at the middle position of its cross-section.

To study the electropolishing behaviour of the Cu deposits in the 40 vol.% H_3PO_4 solution at $25 \pm 1 \text{ }^\circ\text{C}$, we used Cu-deposited Ti-RCEs prepared in the baths with 0, 1, 5 and 8 ppm thiourea. The counter

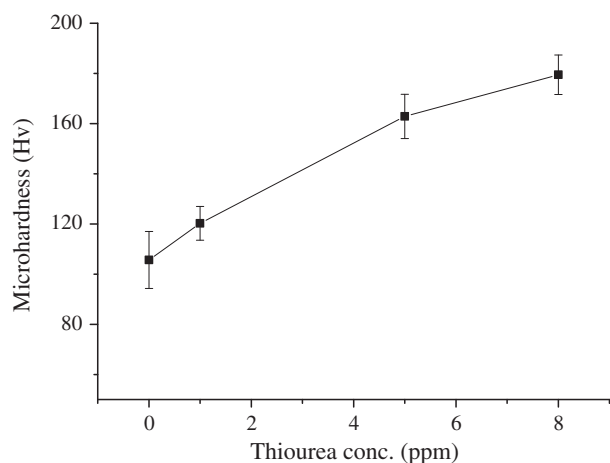


Fig. 2. Hardness and standard deviation values of Cu deposits prepared in the Cu-plating baths with different thiourea concentrations.

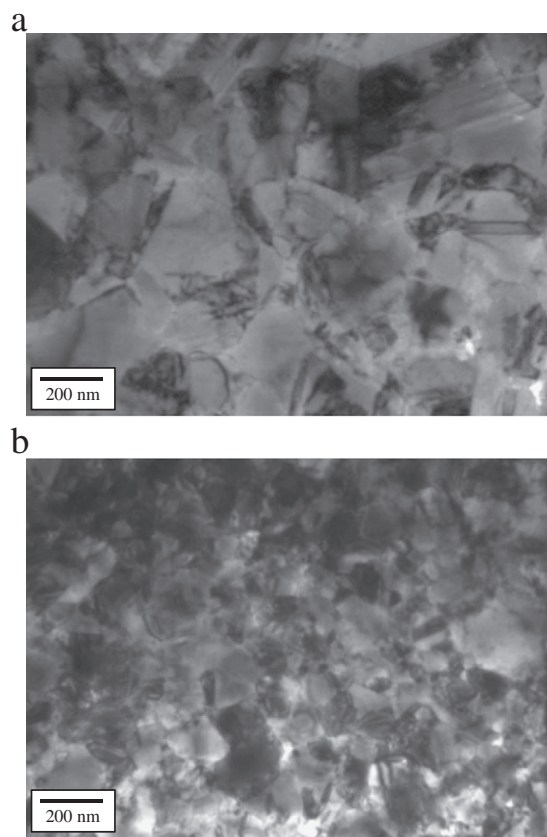


Fig. 3. TEM observations of twin-jet etched Cu deposits prepared in plating baths (a) without and (b) with 8 ppm thiourea.

and reference electrodes were the same as those used in the Cu electroplating. The anodic polarisation behaviour of the Cu-deposited Ti-RCEs was determined in a 40% H_3PO_4 solution at $25 \pm 1 \text{ }^\circ\text{C}$. The results of the anodic polarisation test were used to determine the limiting current plateau at which potentiostatic polishing of the Cu-deposited specimen could be conducted. After electropolishing, the Cu-deposited Ti-RCE was rinsed in water, flushed with alcohol, dried with air blaster and prepared for surface examination. The polished Cu surfaces were examined with a field emission scanning electron microscope (FESEM, JEOL JSM-6701F) and an atomic force microscope (AFM, Molecular Imaging PicoSPM LE).

3. Results and discussion

3.1. Electroplating and hardness test

Fig. 1 shows the variation of the cathodic potential during Cu electroplating in the baths with thiourea up to 8 ppm. Obviously, the cathodic potential increases with an increasing thiourea content in the Cu-plating bath. The cathodic potential was -2.0 V during Cu electrodeposition in the thiourea-free bath. By adding thiourea of 1, 5 and 8 ppm, the cathodic potentials for Cu electrodeposition changed to -2.4 , -2.85 , and -3.15 V , accordingly. This result indicates that the addition of a small amount of thiourea to the Cu-plating bath impedes the formation rate of the Cu deposits. The same effect of thiourea in an acidic Cu-plating bath on the cathodic potential shift was reported by Donepudi et al. [16–18]. They suggested that the cathodic potential shift is attributed to chemisorption of thiourea on the cathode during Cu electroplating.

The hardness values of the Cu deposits prepared in the baths with different thiourea contents are shown in Fig. 2. The hardness of the Cu deposit markedly increased with an increase in the thiourea content in the Cu-plating baths from 106 Hv for the deposit prepared in the

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