

## Relationship between hardness and grain size in electrodeposited copper films

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### Abstract

Copper films were electrodeposited under various conditions and the relationship between the hardness and grain size of the films was investigated. The Vickers hardness depended on the processing conditions. This is because the processing conditions affected the grain size. In particular, nanocrystalline Cu film with a grain size of 31 nm was obtained by optimizing the electrodeposition conditions. The hardness of the nanocrystalline film deviated from the Hall–Petch relationship because the grain size dependence of hardness is smaller for the grain sizes of <100 nm than those of >100 nm. Also, the constants  $Hv_0$  and  $k_{Hv}$  in the Hall–Petch relationship for films processed with thiourea were different from those for films processed with gelatin. The differences may not be related to texture but to superabundant vacancies generated in the process of electrodeposition. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Electrodeposition; Hall–Petch relationship; Cu films; Nanocrystalline Cu; Hydrogen

### 1. Introduction

Copper films and lines are used as interconnections on printed circuit boards, systems in packages and semiconductor devices. Electrodeposition is one of the methods of obtaining metallic films and lines with adequate thickness, porosity-free structure and good adhesion [1–3]. Electrodeposited copper films have been extensively investigated with respect to their morphological characteristics, microstructure, electrical properties and mechanical properties [4–8]. Recently, Yamasaki [9] has reported a nanocrystalline Ni–W alloy showing a high strength of 2300 MPa that was fabricated by electrodeposition, indicating that grain refinement is one of the principal strengthening mechanisms in electrodeposited metallic films. The grain size of electrodeposited metallic films is affected by processing conditions based on parameters such as current density, temperature, electrolyte composition, and substrate type. Therefore, it is important to investigate the relationships among the processing conditions, grain size and mechanical properties for the

enhancement of functional properties of electrodeposited copper films.

In the present study, copper films are electrodeposited under various conditions of the type and concentration of additives (thiourea and gelatin), current density and the substrate type (polycrystalline SUS304 and amorphous Fe alloy). In general, the relationship between hardness and grain size can be given on the basis of the Hall–Petch relationship by

$$Hv = Hv_0 + k_{Hv}d^{-1/2} \quad (1)$$

where  $Hv$  is the hardness in a polycrystalline metal,  $d$  the grain size, and  $Hv_0$  and  $k_{Hv}$  are constants. In the present study, the relationship between the hardness and grain size of electrodeposited copper films is investigated on the basis of the Hall–Petch relationship. In particular, the deviation of a nanocrystalline film from the Hall–Petch relationship and the effects of additives on the constants  $Hv_0$  and  $k_{Hv}$  in the Hall–Petch relationship are focused upon.

### 2. Experimental method

Thin copper films were processed by an electrodeposition technique with an acid copper sulfate bath. The electrolyte

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composition was  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (220 g/l) and  $\text{H}_2\text{SO}_4$  (60 g/l). Thiourea and gelatin were used as additives, where the concentrations were 0.005–0.035 g/l for thiourea and 0.001–0.060 g/l for gelatin. The current densities were 10–150  $\text{mA}/\text{cm}^2$  with dc current. The film specimens, with a thickness of approximately 30  $\mu\text{m}$ , were electrodeposited on a polycrystalline SUS304 or an amorphous Fe alloy substrate plate. The bath temperature was maintained at 23 °C.

The Vickers hardness was measured at room temperature on the polished specimens using a Shimadzu HMV-2000 with a 150 mN indenting load and a 15 s dwell time. The hardness tests were carried out 20 times for each specimen and the average and standard deviation of hardness were obtained.

The texture of the specimens was measured using Rigaku RINT Ultima III X-ray diffraction equipment. The specimens for texture measurement were cut into square-shaped plates each with an area of 30 mm  $\times$  30 mm, and loaded on a pole figure attachment. The pole figure data for (2 2 0) and (1 1 1) were measured with Cu K $\alpha$  radiation in a reflection geometry.

The microstructure of the specimens was investigated by transmission electron microscopy (TEM). The TEM observation was carried out with a JEOL JEM-1200EX at an operating voltage of 100 kV. The specimens for TEM observation were thinned using a dimple grinder and an Ar ion milling. Also, energy dispersive X-ray (EDX) analyses were carried out using a second transmission electron microscope (JEOL JEM-2100F) at 200 kV, equipped with EDX equipment (JED-2300T), to investigate segregation. In addition, the hydrogen concentrations in the specimens were investigated by an inert gas fusion method in an impulse furnace (Horiba EMGA-621). The hydrogen analysis was performed three times on each specimen.

### 3. Results and discussion

#### 3.1. Effects of processing conditions

The variation in the Vickers hardness of the electrodeposited copper films as a function of the concentration of thiourea is shown in Fig. 1, where the current density is 50  $\text{mA}/\text{cm}^2$  and

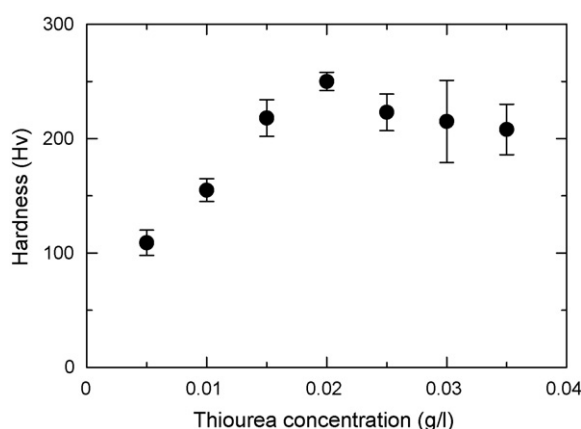


Fig. 1. Variation in Vickers hardness of electrodeposited copper films as function of concentration of thiourea, where current density was 50  $\text{mA}/\text{cm}^2$  and polycrystalline SUS304 was used as substrate.

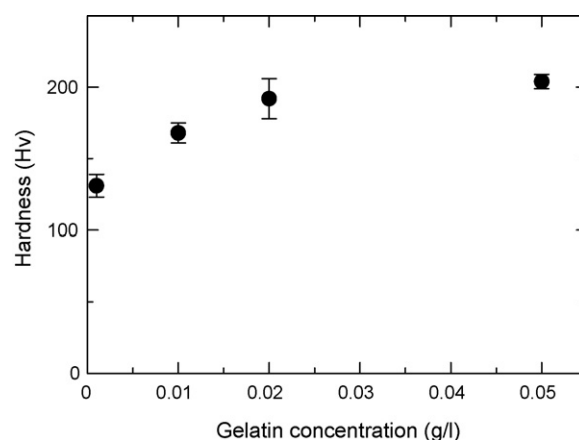


Fig. 2. Variation in Vickers hardness of electrodeposited copper films as function of concentration of gelatin, where current density was 50  $\text{mA}/\text{cm}^2$  and polycrystalline SUS304 was used as substrate.

the substrate is a polycrystalline SUS304. The Vickers hardness increased with increasing thiourea concentration up to 0.020 g/l; however, it gradually decreased with increasing thiourea concentration from 0.020 g/l.

The variation in the Vickers hardness of the electrodeposited copper films as a function of the concentration of gelatin is shown in Fig. 2, where the current density is 50  $\text{mA}/\text{cm}^2$  and the substrate is a polycrystalline SUS304. The Vickers hardness increased with increasing gelatin concentration. When the gelatin concentration exceeded 0.05 g/l, however, holes or pores were formed in the electrodeposited copper film. Thus, there were the optimum concentrations of the additives (0.02 g/l for thiourea and 0.050 g/l for gelatin) for maximum hardness.

Transmission electron micrographs of the electrodeposited copper films with thiourea and gelatin are shown in Fig. 3. No or few dislocations and twins were found in the electrodeposited copper films. Inspection of Fig. 3 reveals that the grain size of the film with thiourea of 0.020 g/l was smaller than that of the film with gelatin of 0.050 g/l. The grain sizes of all the specimens are listed in Table 1. The grain size roughly tended to decrease with an increase in the concentration of additives, with a few exceptions. Additives act as a grain refiner [10–13] because additives such as thiourea inhibit the deposition of copper from sulfate solutions and enhance the nucleation process [12–14]. Therefore, it is likely that an increase in hardness by the addition of thiourea and gelatin is attributed to grain refinement.

Fig. 4 shows the relationship between current density and Vickers hardness in the electrodeposited copper films, where the additive is thiourea (0.020 g/l) and the substrate is an amorphous Fe alloy. The Vickers hardness increased with increasing current density. However, at more than 110  $\text{mA}/\text{cm}^2$ , the surfaces of films were powdery and sound films were not obtained, as shown in Fig. 5. Ibañez et al. [7] reported the same trend; that is, copper deposition became mass-transfer-limited or very close to the mass transfer limit at very high current densities, resulting in powdery surfaces. It can be seen from Table 1 that the increase in hardness with current density is due to grain refinement. Many studies [15–17] showed that the grain size of depositions is reduced with an increase in current density or over-

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