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Comparison of Mechanical Properties of Thin Copper Films Processed by Electrodeposition and Rolling

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Thin copper films with grain sizes of 31 nm and 3.3 μm were processed by electrodeposition, and their mechanical properties were compared with those of a rolled copper film. The hardness and strength for the electrodeposited copper with a grain size of 3.3 μm were lower than those of the rolled copper with a grain size of 6.3 μm, however, the elongation to failure for the former was larger than that for the latter. Intense (111) texture formation was found for the rolled copper. Therefore, it is suggested that the difference in mechanical properties between the electrodeposited and rolled copper films are related to the texture formation. The electrodeposited copper with a grain size of 31 nm showed higher strength and larger elongation than the rolled copper. The very small grain size of 31 nm gave rise to the excellent mechanical properties. [doi:10.2320/matertrans.MAW200708]

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1. Introduction

Electrodeposition is widely used as fabrication method of fine copper lines and films for interconnections of printed circuit boards, systems in package and semiconductor devices. In these applications, it is required to improve the physical and mechanical properties of the fine copper components for the high performance and reliability of interconnections. It is known that mechanical properties of the fine copper deposits are affected by microstructural factors such as texture,[1,2] grain size,[2,3] impurity[4–7] and lattice strain.[8–10] In particular, the grain size effects should be focused on because nanocrystalline metals can be fabricated by electrodeposition route.[11]

One of other methods for fabrication of thin copper films is rolling. In this case, intense texture is often formed. Hence, it is expected that the crystallographic structure such as texture in a rolled copper film is different from that processed by electrodeposition. In the present paper, mechanical properties of thin copper films, with different grain sizes, processed by electrodeposition are investigated by hardness tests and tensile tests, and they are compared with those of a thin copper film processed by rolling. In addition, the difference in mechanical properties is discussed from the viewpoint of a grain size, texture and hydrogen concentration.

2. Experimental

Thin copper films were processed by electrodeposition technique with an acid copper sulfate bath ($CuSO_4{\cdot}5H_2O$ 220 g/L and H_2SO_4 60 g/L). A fine-grained copper film was electrodeposited with an additive of 0.02 g/L thiourea and with the direct-current electricity density of 1000 A/m^2 on an amorphous Fe alloy substrate plate. Also, a coarse-grained copper film was electrodeposited with no additive and with the direct-current electricity density of 500 A/m^2 on a polycrystalline SUS304 substrate plate. The bath temperature was kept at 296 K during electrodeposition process. The thickness of the copper films obtained was 30 μm. For comparison, a commercial rolled thin copper film with a thickness of 30 μm was purchased.

The Vickers hardness was measured on the polished specimens by using a Shimadzu HMV-2000 with indenting load of 150 mN and dwell time of 15 s. Dog-bone-shaped specimens with 9.0 mm in gage length, 2.0 mm in gage width and 30 μm in gage thickness for the tensile tests were prepared by an electro-discharge machine. The tensile tests were conducted at a crosshead speed of 1.0 mm/min and at room temperature by a Shimadzu AUTOGRAPH AG50kN-G.

Microstructure of the films was investigated by transmission electron microscope (TEM). The TEM observation was carried out with a JEOL JEM-1200EX with an operating voltage of 100 kV. The specimens for TEM observation were thinned by using a dimple grinder and an Ar ion milling. Also, textures of the specimens were measured by using Rigaku RINT Ultima III X-ray diffraction equipment. The specimens for texture measurement were cut to be a square shape plate with 30×30 mm^2, and loaded on a pole figure attachment. The (111) pole figure data were measured with CuKα radiation in reflection geometry. In addition, the hydrogen concentrations in the films were investigated by using Horiba EMGA-621. The hydrogen measurements were performed three times on each specimen.

3. Results and Discussion

Transmission electron micrographs of the electrodeposited

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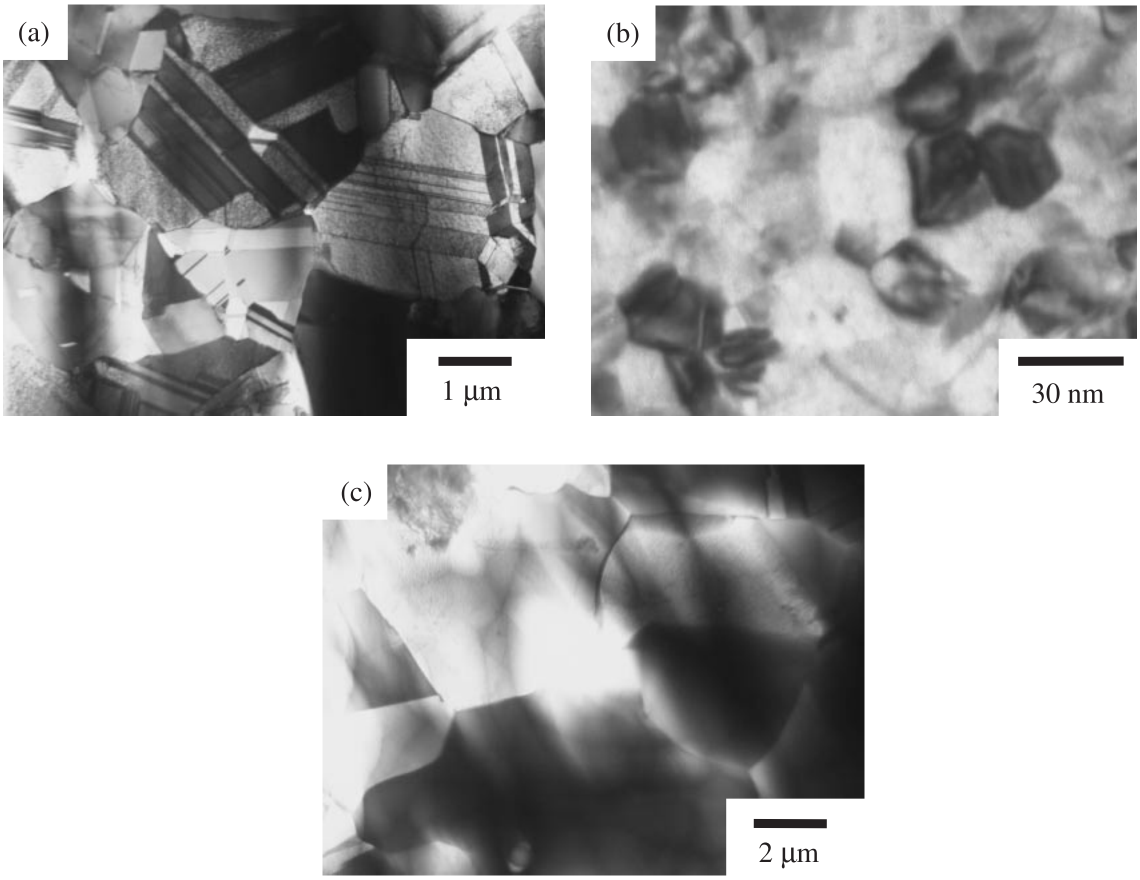

Fig. 1 Transmission electron micrographs of copper films, (a) the electrodeposited copper film with no additive at the current density of 500 A/m^2 on a polycrystalline SUS304 substrate, (b) the electrodeposited copper film with thiourea of 0.02 g/L at the current density of 1000 A/m^2 on an amorphous Fe alloy substrate, and (c) the rolled copper film.

Table 1 The Vickers hardness of the electrodeposited copper films and the rolled copper film.

	Electrodeposited copper with a grain size of 3.3 μm	Electrodeposited copper with a grain size of 31 nm	Rolled copper
Average hardness and standard deviation (Hv)	100 ± 7	266 ± 8	141 ± 4

and rolled copper films are shown in Fig. 1. A grain size was 3.3 μm for the electrodeposited copper with no additive at the current density of 500 A/m^2 on a polycrystalline SUS304 substrate, and 31 nm for the electrodeposited copper with thiourea of 0.02 g/L at the current density of 1000 A/m^2 on an amorphous Fe alloy substrate, respectively. Also, a grain size of the rolled copper was 6.3 μm. Note that a nano-crystalline copper with a very small grain size of 31 nm was obtained by electrodeposition method.[11)]

Inspection of Fig. 1 reveals that there were twins in the electrodeposited copper with a grain size of 3.3 μm, on the other hand, few twins were found in the electrodeposited copper with a grain size of 31 nm and the rolled copper. Also, few dislocations were found, and there were no pores in all the films.

The results of hardness tests for the copper films are summarized in Table 1. The hardness for the electrodeposited copper with a grain size of 31 nm was very high. On the other hand, the hardness for the electrodeposited copper with a grain size of 3.3 μm was lower than that for the rolled copper.

Figure 2 shows the nominal stress-strain curves by tensile tests for the electrodeposited and the rolled copper films. The 0.2% proof stress and ultimate tensile strength were 242 and 294 MPa for the electrodeposited copper with a grain size of 3.3 μm, and 348 and 364 MPa for the rolled copper, respectively. As shown in Fig. 1, a grain size of the rolled copper (= 6.3 μm) was larger than that of the electro-deposited copper (= 3.3 μm), and there were few twins and dislocations in the rolled copper. Thus, higher strength for the rolled copper cannot be explained from the differences in grain size, twins and dislocations.

The (111) pole figure data are shown in Fig. 3, where the arrows indicate the loading direction in tensile tests. Intense (111) texture formation was found for the rolled copper. This is in agreement with the previous studies.[12,13)] However, the intensity of (111) texture was much weaker in the electro-deposited copper films. For the rolled copper (Fig. 3(c)),

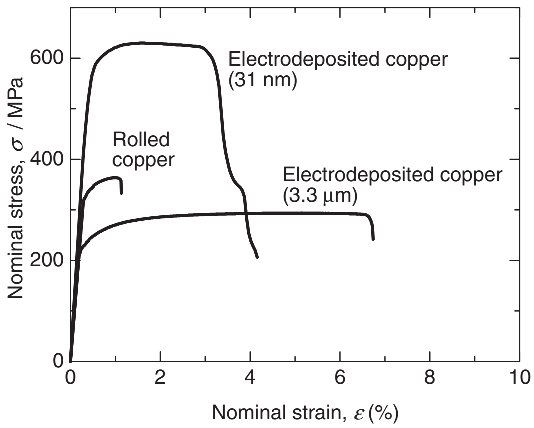

Fig. 2 Nominal stress-nominal strain curves by tensile tests at room temperature for the electrodeposited copper films with grain sizes of 3.3 μm and 31 nm and the rolled copper film.

there were two peaks of intense (111) texture. The tensile direction was roughly perpendicular to the normal lines for the two peaks in the rolled copper. Therefore, it is conclusively demonstrated that the higher strength for the rolled copper is attributed to the intense texture formation because of the low Schmid factor.

In general, elongation to failure of bulk copper is more than 30%.[14,15] However, the thin copper films had much poorer tensile ductility, compared to bulk copper. Uchic *et al.*[16] showed that the sample dimension drastically influences the strength. Arzt *et al.*[17] also discussed mechanisms of the size effect from the viewpoint of interface controlled plasticity. The fact that the thin copper films had much poorer tensile ductility than bulk copper indicates that the inherent crystal plasticity in thin film metals affects not only strength, but also ductility, independently of the texture and grain size. Hence, ductility is one of critical mechanical properties in thin copper components.[18] As shown in Fig. 2, an elongation to failure for the electrodeposited copper with a grain size of 3.3 μm was 6.7%, and that for the rolled copper was only 1.1%. This indicates that the texture has a strong effect on ductility as well as strength.

One of other origins for the large differences in mechanical properties between the electrodeposited and the rolled coppers may be the presence of impurities, in particular, hydrogen.[4,7] Table 2 shows the concentrations of hydrogen in the electrodeposited copper with a grain size of 3.3 μm and the rolled copper. The average value of hydrogen concentration in the electrodeposited copper was about twice larger than that in the rolled copper. Okinaka *et al.*[4] showed that ductility of electroless copper is decreased with increasing

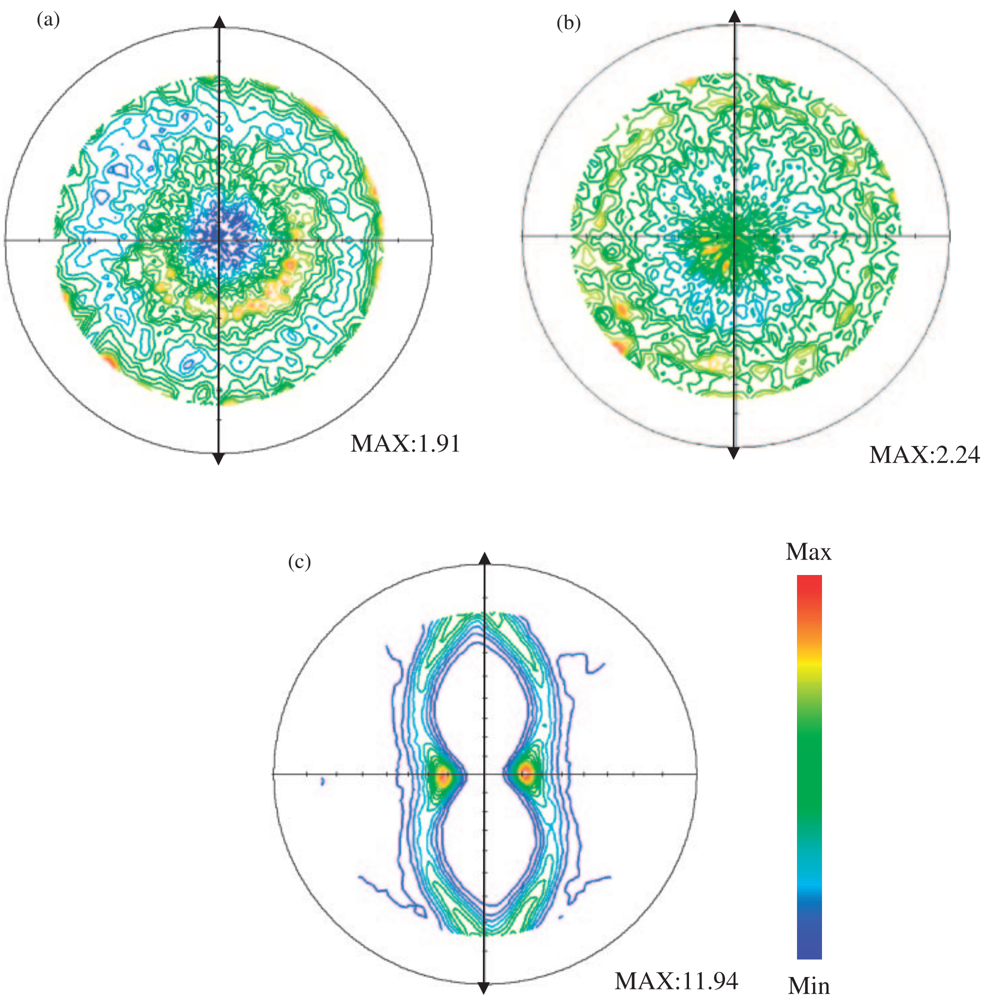

Fig. 3 Pole figures of (111) plane of copper films. (a) The electrodeposited copper film with a grain size of 3.3 μm, (b) the electrodeposited copper film with a grain size of 31 nm and (c) the rolled copper film. Arrows indicate loading direction in tensile tests.

Table 2 Concentrations of hydrogen in the electrodeposited copper film with a grain size of 3.3 μm and the rolled copper film.

		Hydrogen concentration (ppmw)
Electrodeposited copper with a grain size of 3.3 μm		8.16
		4.74
		5.96
	average	6.29
Rolled copper		3.18
		3.42
		3.16
	average	3.25

hydrogen concentration. In the present study, however, the elongation of the electrodeposited copper was larger, in spite of the higher hydrogen concentration. Therefore, it is suggested that effect of hydrogen on mechanical properties is minor.

Valiev[19] showed that a nanocrystalline metal exhibits high strength and high ductility. Note that the electrodeposited copper with a grain size of 31 nm showed higher strength and larger elongation than the rolled copper. The very small grain size of 31 nm gave rise to excellent mechanical properties of high strength and high ductility. However, the elongation of the electrodeposited copper with a grain size of 31 nm was lower than that of the electrodeposited copper with a grain size of 3.3 μm. Yamasaki[20] showed that nanocrystalline nickel films produced by electrodeposition exhibited very low elongation of less than 1%. Hence, it is likely that grain refinement does not necessarily give rise to significant enhancement of tensile ductility. In general, strain hardening inhibits local necking and thus promotes uniform straining, resulting in large tensile elongation. Wang *et al.*[21] showed that tensile ductility of a nanocrystalline metal strongly depends on strain hardening behavior. Inspection of Fig. 2 reveals that the strain hardening coefficient for the electrodeposited copper with a grain size of 31 nm is lower than that the electrodeposited copper with a grain size of 3.3 μm. Therefore, the poorer tensile ductility for the former may be attributed to the lower strain hardening. Further research is needed to understand the origin of poor tensile ductility of the nanocrystalline metals produced by electrodeposition.

4. Conclusions

Mechanical properties of thin copper films processed by electrodeposition were investigated by hardness tests and tensile tests, and they were compared with those of a rolled copper film. The results are summarized as follows.

(1) The hardness and strength for the electrodeposited copper with a grain size of 3.3 μm were lower than those of the rolled copper with a grain size of 6.3 μm. On the other hand, the elongation to failure for the former was larger than that for the latter.

(2) Intense (111) texture formation was found for the rolled copper. Therefore, it is suggested that the difference in mechanical properties between the electrodeposited and rolled copper films are attributed to the difference in texture.

(3) The electrodeposited copper with a grain size of 31 nm showed higher strength and larger elongation than the rolled copper. The excellent mechanical properties of the electrodeposited copper are mainly attributed to the very small grain size of 31 nm.

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