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Effects of Ultrasound on Morphology of Copper Electrodeposited on Titanium in Aqueous and Organic Solutions

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The copper films were electrodeposited from aqueous and organic solutions in the presence and in the absence of ultrasound. The internal stress and texture in copper films were studied using the X-ray diffraction (XRD). The results showed that the internal stress and texture of the copper films were reduced on the effect of ultrasound. The surface morphology of copper grains was investigated using scanning electron microscopy (SEM). The results showed that the porous structure was formed on the surface of copper grains deposited in organic solution under ultrasonic radiation. [doi:10.2320/matertrans.MRA2007157]

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1. Introduction

The benefits of ultrasound to electrochemical process have been recognized and explored for a long time.[1] Ultrasound is known for its capacity to promote especially heterogeneous reactions mainly through extremely increased mass transport, interfacial cleaning, and thermal effects.[2] In general, the imposition of ultrasound in electrodeposition systems gives rise to an increase of effective current density, improvement of deposition rate and changes in chemical and physical properties of deposited metal film.[3–5] The performance and reliability of electrodeposited copper films are influenced by internal stress and texture. Significant changes in microstructure occur due to the application of ultrasound. The porous structure of copper film formed in organic solution was different from the porous structure obtained at high overpotential.[6] The average diameter of the pores was about 30 nm, and the wall of which was compact under ultrasound.

The present paper reported the effect of ultrasound on the internal stress, texture and morphology of electrodeposited copper films. The copper films were prepared in aqueous and organic solutions, respectively. The internal stress and texture of the films were investigated using XRD method, and the surface morphology of copper grains using SEM method.

2. Experimental

The compositions of aqueous and organic solutions were same, 150 g/L of $CuSO_4$ + 200 g/L of H_2SO_4. The solvent of organic solution was glycol. The substrate was a titanium plate of 3 cm × 3 cm × 1 cm. It was polished with emery paper, etched with HF for several seconds, rinsed with distilled water, dried with ethanol, and then electrodeposited immediately. Experiments were performed with a 120 W frequency generator from electronic service at a fixed frequency of typically 40 kHz, in a cell filled with 100 ml bath. The ultrasonic transducer was placed at the bottom of the cell.

X-ray diffraction (XRD) technique was used to investigate the internal stress and the texture of copper films. X-ray diffraction analysis was carried out using a Model Dmax/rC X-ray Diffractometer, using the CuKα Scattering was measured from $2\theta = 30$ to 100° at intervals of 0.02°. The internal stress in specimens was investigated by the well-known $\sin^2\psi$ X-ray diffraction method. The parameters of stress analyzer were: Cr-Kα radiation, diffraction plane Cu(220), step speed 1°/min, ψ angle 0°, 24°, 35° and 45°. The surface morphology of copper deposit was observed by using FEI SIRION 200 FE-SEM.

3. Results and Discussion

3.1 Stress and texture

In organic solution, the copper films were difficult to be electrodeposited without ultrasound. Many incompact copper powders were deposited on the substrate. So, three kinds of copper films were prepared in different electrolytes, (a) in organic solution with ultrasound, (b) in aqueous solution with ultrasound and (c) in aqueous solution without ultrasound. Figure 1. showed the results of internal stress of electrodeposited copper films. The internal stress of the films was

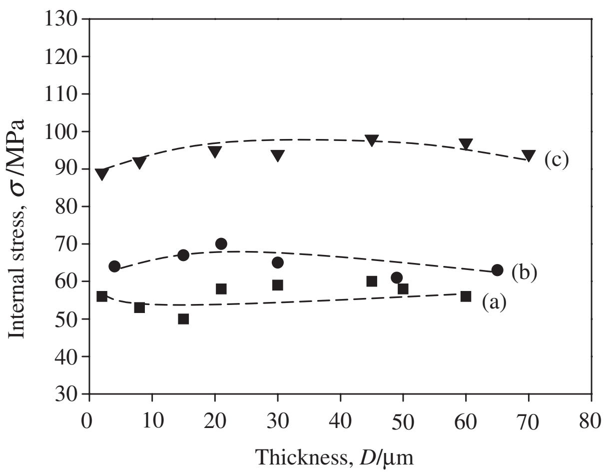


Fig. 1 Inference of ultrasound on the internal stresses of copper films. (a) in organic solution with ultrasound (b) in aqueous solution with ultrasound (c) in aqueous solution without ultrasound.

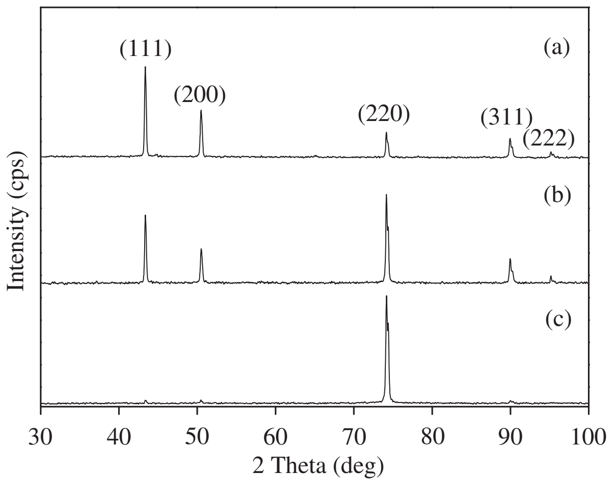


Fig. 2 X-ray diffraction patterns for electrodeposited copper films. (a) in organic solution with ultrasound (b) in aqueous solution with ultrasound (c) in aqueous solution without ultrasound.

always tensile. The stress of copper film electrodeposited in aqueous solution was decreased on the effect of ultrasound. The absorption of water vapor was considered that it was one of the sources caused the internal stress of the electrodeposited films.[7] The effect of ultrasonic cavitation and micro-jet can reduced the absorption of water vapor in the copper films. The stress of copper films deposited in aqueous and organic solutions was decreased and had the same level due to the effect of ultrasound.

Figure 2 showed the XRD patterns for the copper films electrodeposited in aqueous and organic solutions, respectively. It is obviously seen that the copper films deposited in aqueous electrolyte without ultrasound had highly (220) preferred orientation. From surface energy consideration, the closest-packed-planes should be favored. Films of fcc metals often exhibit a (111) texture. However, according to the point of view of strain energy minimization, the grains with (220) orientation should be favorable in the films.[8–10] Copper films an support high strain energy density. So, the change of the fiber texture, from surface energy minimizing type to strain energy minimizing type, may take place with the increase of stress in the films.

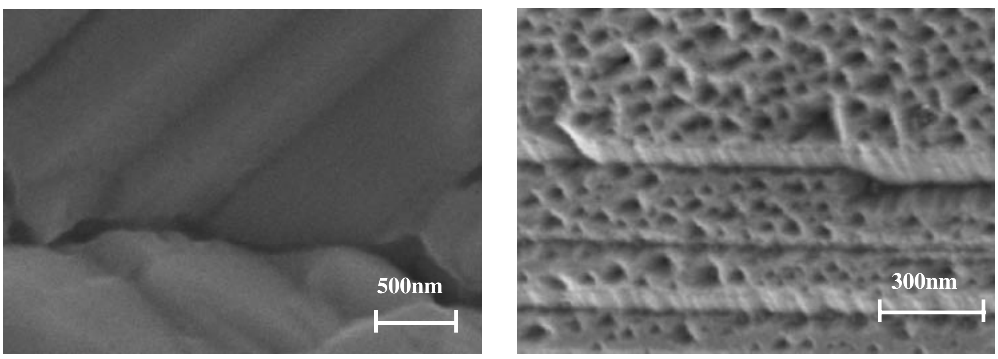
The (220) texture of the copper films deposited in aqueous and organic electrolytes was obviously reduced when the ultrasound treatment was carried out. According to the result of the internal stress, the stress was decreased on the effect of ultrasound. So, the influence of the strain energy on the grains orientation was reduced with the decrease of the stress. It resulted in the decrease of the extent of (220) preferred orientation.

3.2 Surface morphology

Hydrogen bubbles as a result of the chemical reactions were the main byproducts in the electrodeposition process. The hydrogen bubbles originated from the cathodic reaction on substrate. Where there is a bubble, there will be no deposition of metals because there are no metal ions available. In the aqueous solution, the bubbles can rapidly remove from the deposition site. The hydrogen bubbles were difficult to diffuse in the organic solution and it is one of the reasons why the copper film can not be electrodeposited in the organic solution without ultrasound.

In the aqueous solution, the ultrasonic vibration plays an important role in ensuring mass transport at the surface of the substrate. This enhanced mass transport presents the advantages of almost-instant bubble removal and rapid replenishment of the electrolyte in the gap. The effect of ultrasound was useful to increase the current efficiency and brightness of the electrodeposited copper films.[11] Figure 3 showed the surface morphology of copper grains deposited with ultrasound in aqueous and organic electrolytes. As shown in Fig. 3(a), the surface of copper grains was smooth.

The porous structure was observed in the copper films deposited in organic solution. As shown in Fig. 3(b), the average size of these pores approached nano-size dimensions. The size of the hydrogen bubble originated from substrate decreased because of the effect of acoustic streaming. At the same time, the ultrasound promoted the diffusion of the hydrogen bubble, increased the effective current density and improved the deposition rate. It is useful to deposition of copper films. The concentration of metal ions in the vicinity of the metal deposits was quickly depleted when the deposition rate was sufficiently high. Incessant bubble evolution disrupts the diffusion of reactive ions from bulk electrolyte to ion-depleted region. Consequently, many pores were formed on the surface of copper grains.



(a) (b)

Fig. 3 SEM images of copper films electrodeposited with ultrasound in aqueous and organic solutions: (a) aqueous solution, (b) organic solution.

The porous structure reported in this paper was different from the porous structure electrodeposited at high overpotential. In general, the size of the surface pores deposited at high overpotential was about 50 μm and the walls of the pores exhibited dendrite.[12,13] The average diameter of the pores obtained in the organic solution on the effect ultrasound was about 30 nm and the walls of the pores were compact. The hydrogen bubbles on the surface of copper grains were not spherical because of the effect of ultrasonic micro-jet. So the pores formed in the organic electrolyte were not spherical.

4. Conclusions

In the paper, internal stress, texture and morphology of electrodeposited copper films were investigated in both aqueous and organic solutions. The internal stresses (stress) of the films deposited with ultrasound were (was) decreased on the shock effect from ultrasonic cavitation and micro-jet. The extent of (220) preferred orientation of the films deposited with ultrasound was reduced as a result of the decrease of the stress. It was observed that the porous structure was formed on the surfaces of the copper grains deposited with ultrasound in organic solution. It provided a new approach to get the porous structure.

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REFERENCES

1) R. G. Compton, J. C. Eklund, F. Marken, T. O. Rebbitt, R. P. Akkermans and D. N. Waller: Electrochimica. Acta. **42** (1997) 2919.
2) S. V. Ley and C. M. R. Low: *Ultrasound in Synthesis* (Spring, Berlin, 1989).
3) A. Chiba and W. C. Wu: Plat. Surf. Finish. **79** (1993) 62.
4) P. B. S. N. V. Prasad, R. Vasudevan and S. K. Seshadri: Trans. Indian. Inst. Met. **46** (1993) 247.
5) R. Walker and N. S. Holt: Plat. Surf. Finish. **68** (1981) 44.
6) N. D. Nikolic, K. I. Popov, L. J. Pavlovic and M. G. Pavlovic: Surf. Coat. Technol. **201** (2006) 560.
7) P. Gudmundson and A. Wikstrom: Microelectronic Engineering. **60** (2002) 17.
8) R. Carel, C. V. Thompson and H. J. Frost: Acta. Mater. **44** (1996) 2479.
9) J. M. Zhang and K. W. Xu: J. Mater. Sci. Lett. **18** (1999) 471.
10) J. M. Zhang, K. W. Xu and V. Ji: Appl. Surf. Sci. **180** (2001) 1.
11) R. Vasudevan and R. Devanathan: Met. Finish. **90** (1992) 23.
12) H. C. Shin, J. Dong and M. Liu: Adv. Mater. **19** (2003) 1610.
13) H. C. Shin and M. Liu: Chem. Mater. **16** (2004) 5460.