Journal of The Electrochemical Society, **149** (9) G535-G538 (2002)

0013-4651/2002/149(9)/G535/4/$7.00 © The Electrochemical Society, Inc.

The Effect of Plating Current Densities on Self-Annealing Behaviors of Electroplated Copper Films

Shih-Chieh Chang,[a] Jia-Min Shieh,[b,z] Bau-Tong Dai,[b] Ming-Shiann Feng,[a] and Ying-Hao Li[c]

[a]*Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan*
[b]*National Nano Device Laboratories, Hsinchu 30050, Taiwan*
[c]*Merck-Kanto Advanced Chemicals Limited, Taipei, Taiwan*

In this study, the effect of plating current densities on self-annealing behaviors of electroplated Cu films was found to be relevant to the polarization resistance of electroplating systems. Porous films with defects occurred at low plating current density or at low polarization resistance. In contrast, dense films with small grains occurred at higher plating current density or at higher polarization resistance. However, when more current was further supplied, Cu aggregation occurred and deposited films became spongy or dendritic. We suggest that both the defects within porous films and the underlying energy of fine-grained deposits accelerated self-annealing. These two characteristics competed with each other to determine the resistivity drop by self-annealing. On the other hand, the (111) texture evolutions of deposited Cu films with an increase of plating current densities were consistent with the evolutions of resistivity and surface morphology.
© 2002 The Electrochemical Society. [DOI: 10.1149/1.1500348] All rights reserved.

Manuscript received January 4, 2002. Available electronically August 1, 2002.

Electroplating is emerging as one choice for Cu metallization in multilevel interconnects because of its superior ability to fill the submicrometer trenches and vias of damascene architectures as compared to other techniques, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD).[1] Another advantage for the selection of electroplating is its larger-grained microstructure that can further improve the electromigration resistance. Ryu and co-workers[2] have recently shown that large-grained electroplated Cu has about one order of magnitude higher electromigration resistance than the small-grained chemical vapor deposited Cu. Electroplated Cu films are typically deposited at room temperature by a galvanostatic or a potentiostatic process, and may be metastable immediately after deposition. The as-deposited films will transform through recrystallization to larger-grained structures at room temperature. This is called self-annealing, which has been observed to take place over a period of hours or days after deposition.[3,4] The effect of self-annealing leads to changes in the electrical, mechanical, and microstructural characteristics of deposited films. One intriguing effect of self-annealing was an obvious drop of resistivity of as-deposited electroplated Cu after a transient period of hours at room temperature.[5-7] Several mechanisms that could drive such a transformation have been proposed. These include defects, grain-boundaries, second-phase particles, and surface energies, but also chemical gradients in the material that can cause diffusion-induced grain-boundary migration.[8] In particular, many researchers[9,10] have mentioned that the formation of crystalline defects increased with the elevated biased current and accelerated self-annealing after electroplating. In this study, however, we found that the rate of self-annealing was not simply proportional to plating current densities. We suggest that the microstructure transformation of Cu deposits was driven by two sources. One is the defect within a porous film and the other is the driving force originating from the higher grain boundary energy of a finer-grained deposit.

In addition to grain size, another important influence on electromigration resistance may be the crystallographic texture of the Cu. For Al interconnects, a (111) fiber texture and bamboo-like microstructure have been correlated with improved electromigration performance.[11,12] Several research groups[13-15] have shown that plating and processing conditions have a strong influence on the texture evolution of electroplated Cu. In this article, we discuss the effect of plating current densities on self-annealing behaviors and textures of blanket electroplated Cu films.

[z] E-mail: jmshieh@ndl.gov.tw

Experimental

The blanket wafer for this study was prepared by depositing a 50 nm sputtered TaN diffusion barrier and a 50 nm sputtered Cu conduction layer on a SiO_2/Si substrate. In Cu electroplating processes, the films were deposited under galvanostatic control at room temperature. The crystallographic texture of Cu films was analyzed by X-ray diffraction (XRD). The morphology and the thickness of deposited films were examined by field emission scanning electron microscope (FESEM). The sheet resistance of Cu deposits was measured by a four-point probe measurement. The grain size and surface roughness were measured by atomic force microscope (AFM) of DI Nanoscope.

Results and Discussion

The behavior of electroplated Cu differs from the usual behavior of sputtered Cu, in which no dramatic changes occur at room temperature unless additional stored energy is present. Electroplated Cu thin films can undergo spontaneous abnormal grain growth at room temperature. Microstructure evolution occurs during a transient period of hours following deposition, and includes an increase in grain size, changes in preferred crystallographic texture, and decreases in resistivity, hardness, and compressive stress.[11-15] One reasonable model was based on grain boundary energy in the fine-grained as-deposited films providing the underlying energy that drives abnormal grain growth.[16,17] A number of studies[13-15] have reported on the effect of the bath temperature, current density, bath concentration, etc., on morphologies and textures, but the effect of plating current densities on textures and self-annealing behaviors has not been well understood.

In our previous work,[18] we demonstrated the polarization effect on microstructure evolution and filling capability with an increase of plating current density. According to the range of the current density, the electroplating process can be divided into two regions of mechanisms. When electroplating is under a lower current regime, the electrocrystallization process is a charge-transfer controlled dominant reaction. As the bias current is increased, a mass-transfer controlled dominant reaction takes over until the limiting current density is reached; finally, the reaction is pure mass transfer controlled. In this study, we suggest that the polarization resistance also influences the rate of self-annealing. Figure 1 displays the proposed model of a microstructure evolution with an increase of plating current densities and polarization resistance. Porous or less dense films with defects occurred at low plating current density or at low polarization resistance, as shown in Fig. 1a, then the defects of porous films accelerated resistivity drop. When the defects within porous films decreased with an increase of plating current densities and

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

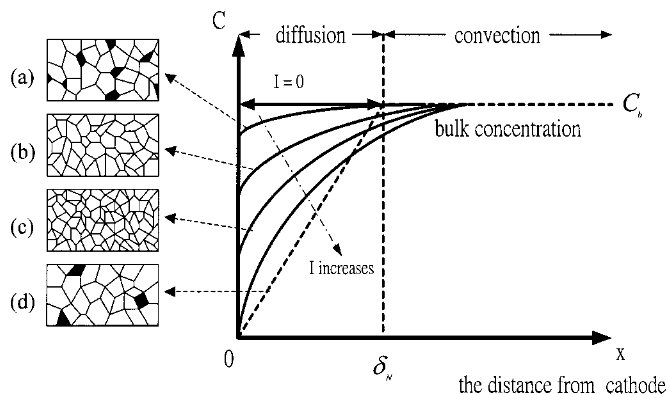

Figure 1. The proposed model of the relationship between self-annealing with polarization effect.

polarization resistance, as can be seen in Fig. 1b, the rate of self-annealing was slowed down. Continuously, when adequate current density was supplied with sufficient polarization resistance, dense deposits with smaller grains enhanced the resistivity drop by the driving force for relaxing the grain boundary energy, as shown in Fig. 1c. However, when more current was further supplied, Cu aggregation occurred and deposits became spongy or dendritic. Then the defects accelerated self-annealing appeared, as shown in Fig. 1d. Figure 2 shows the resistivity evolution with time and compares the films plated at different plating current densities in the electrolyte-containing Cu sulfate (30 g/L), sulfuric acid (275 g/L), and chloride ion (100 ppm). The electrical resistance of a thin blanket film was typically used to probe impurity incorporation and microstructure evolution. Those five curves (a-e) in Fig. 2 represent resistivity drops of Cu deposited at 1, 3.33, 6.67, 10, and 16.67 mA/cm^2, respectively. It can be seen that the resistivity drop by self-annealing was largest at the lowest current density (curve a of Fig. 2), and it decreased to a minimum value with an increase of plating current densities (curve a-c of Fig. 2). In general, porosity in a film is associated with defects generated during deposition and porous films occur at low plating current density or at low polarization resistance. Therefore, the defects of porosities drove self-annealing and promoted resistivity drop. However, when the defects within porous films decreased with plating current densities, the self-annealing velocity was slow down. Therefore, the quantity of defects eventually responds to the resistivity of as-deposited films. Figure 3 shows the resistivity and average surface roughness (Ra) evolutions of as-deposited films with plating current densities. We found that the

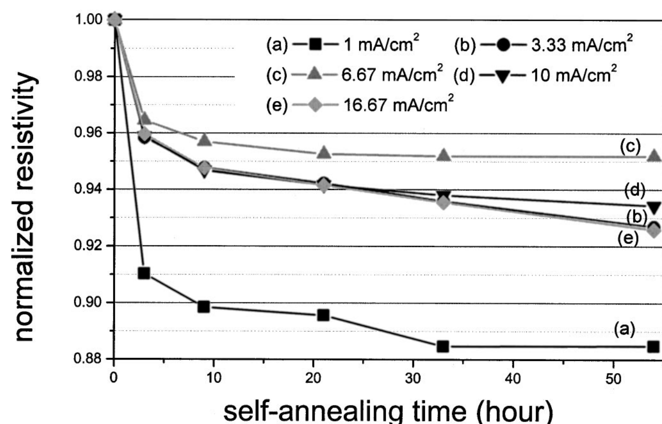

Figure 2. The resistivity evolution with time and comparison of the films plated at different dc densities for the electrolyte containing Cu sulfate (30 g/L), sulfuric acid (275 g/L), and chloride ion (100 ppm).

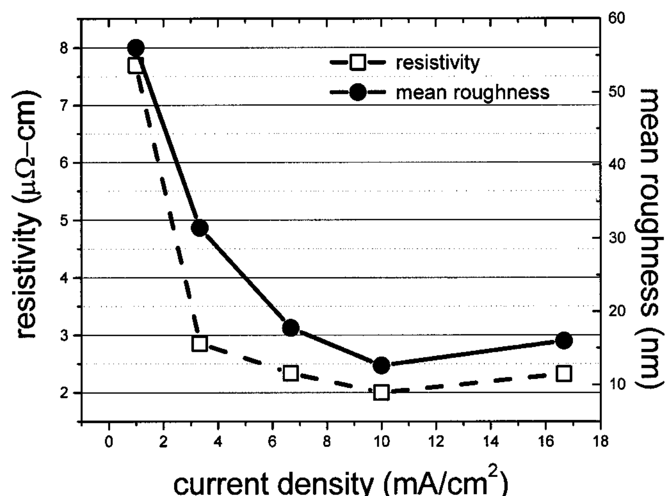

Figure 3. The effect of plating current densities on surface roughness and resistivity of as-deposited Cu films.

abrupt drop of resistivity (7.70 to 2.86 $\mu\Omega$ cm) and average surface roughness (56.10 to 31.43 nm) when the plating current density increased from 1 to 3.33 mA/cm^2. The assistant evidence of decreasing porosity with plating currents was obtained in Fig. 3. This phenomenon was first observed and seen to be different from accelerating self-annealing as an increase of the bias current density, which was mentioned by several groups.[9,10] On the other hand, the perfect gap-filling performance of Cu electroplating in high aspect ratio gaps was usually operated at lower plating current densities. In our previous study,[18] we demonstrated that a higher filling capability was operating in a lower current regime and the filling capability was inversely proportional to the plating current densities (0.33-6.67 mA/cm^2). So far, this finding was valuable for optimizing the super-filling abilities and electrical characteristics of plated Cu.

Continuously, when further high current density was supplied (curve c to d of Fig. 2), the resistivity drop increased again. This can be understood as an increase of the current density enforced the polarization effect and thus enhanced the Cu nucleation process, which promotes the formation of denser Cu films and gives uniform grain distribution, resulting in a lower resistivity Cu film, as shown in Fig. 3.[19,20] Therefore, the underlying energy of the finer-grained deposits (curve d *vs.* curve c) enhanced self annealing. This observation was similar to the investigations of Haebum *et al.*[9] According to the principles of electrocrystallization, the rate of formation of new nuclei on the electrode surface increases exponentially as the cathodic polarization η increases[19,20]

$$\omega = B \exp\left(-\frac{K}{\eta^2}\right) \qquad [1]$$

where the constants B and K are specific for a given metal and temperature. If all other factors remain constant, the increase of cathodic polarization will result in a larger number of newly formed nuclei and a smoother deposit. Figure 3 displays that the resistivity and Ra of as-deposited Cu films decreased with an increase of plating current densities until a threshold current density was reached, and then increased with an increase of plating current densities.

The SEM cross section of Fig. 4 also shows that the Cu film deposited at 10 mA/cm^2 was denser than the film deposited at 3.33 mA/cm^2. But a porous film occurred again when the plating current density was increased to 16.67 mA/cm^2. Furthermore, the mean grain size measured by atomic force microscopy (AFM) also decreased with an increase of plating current densities, but increased when more current was supplied, as can be seen in Fig. 5. For grain

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

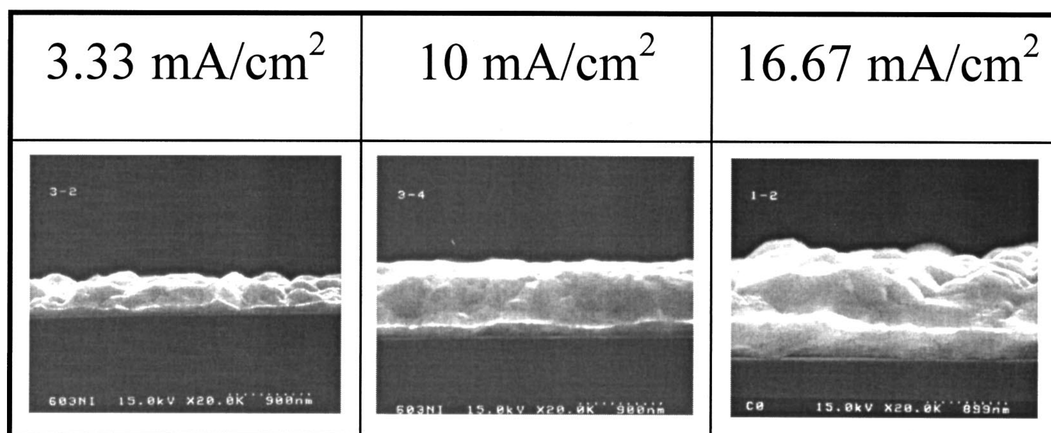

Figure 4. The cross section of Cu films deposited by the additive-free electrolyte with different plating current densities: (a) 3.33, (b) 10, and (c) 16.67 mA/cm^2.

growth, the stored energy decreases with an increase of the growing grain size, and the grain boundary velocity is inversely proportional to the average grain size.[17] This also can explain the phenomenon that the self-annealing effect of the film deposited at 10 mA/cm^2 was faster than the film deposited at 6.67 mA/cm^2, as shown in Fig. 2.

When more current was further supplied, the depletion of cupric ions in the diffusion layer near the cathode surface became severe. Therefore, cupric ions were more difficult to replenish instantly from the solution into the diffusion layer.[13,14] In addition, since cupric ions were reduced very fast and Cu aggregation occurred around the protrusion on the surface under higher electric field, the morphology of deposits became spongy or dendritic. Concurrently, the crystalline defects accelerated self-annealing. In a previous study,[9] Haebum and co-workers found the visible evidence of those defects, and they demonstrated that the density of dislocation loops, which could accelerate the self-annealing process, increased with plating current densities (3.5 to 40 mA/cm^2).

According to the above discussion, we suggest that both the defects of less dense packing deposits and the underlying energy of fine-grained deposits accelerated self-annealing. Therefore, there were two characteristics competing with each other to determine the velocity of self-annealing. Figure 6 also shows the rate of resistivity evolution with time and compares this rate for the films deposited at an equal number of coulombs (average film thickness was about 450 nm). The results are consistent with the trend of Fig. 2.

The crystallographic texture of Cu is face-centered-cubic (fcc) and (111) is the closed packed plane in fcc structures. Therefore, (111) has higher electromigration resistance than other planes of the fcc structure. In fcc thin films, the (111) texture is favored by the surface and interfacial energy minimization, whereas the (200) texture is favored by the strain energy minimization.[17] The observed textures may result from a competition between these mechanisms as mentioned. In Fig. 7, X-ray diffraction (XRD) analyses show the textures of deposits varied with plating current densities. We see that electroplated Cu films had a strongly preferred orientation of (111). In Fig. 5, we also can find that the intensities of Cu(111) peaks increased with an increase of plating current densities, then decreased when more current was supplied. This is because when the deposit plane is oriented normal to the electric field direction, its texture or preferred orientation is symmetrical to the field direction or its growth direction, and is defined by the crystal orientation of the growth direction. Lee and co-workers demonstrated that the texture of electrodeposits changes from the orientation that places the lowest energy crystal facets parallel to the substrate under a condition of the lower ion concentration adjacent to the deposit, to the orientation that places the higher energy crystal facets parallel to the substrate as the higher ion concentration adjacent to the deposit increases.[13,14] An increase of plating current densities decreases the cupric ion concentration adjacent to the cathode, because the depletion rate of cupric ion due to reduction at the cathode is higher than the diffusion rate of cupric ion to the cathode, as can be seen in Fig. 1. Since the (111) plane is the lowest surface energy plane for Cu, an

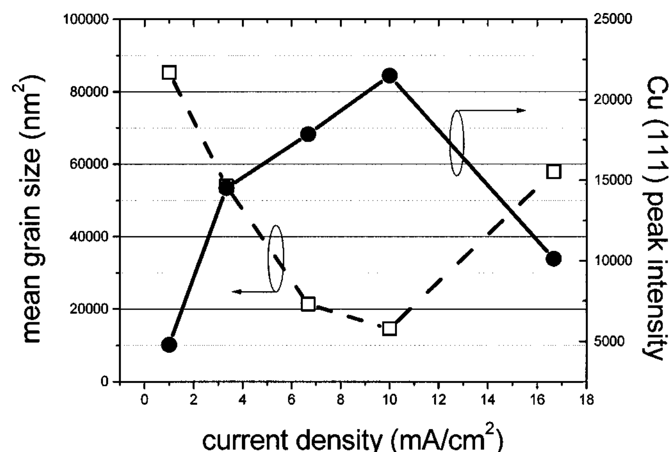

Figure 5. Dependence of current densities on grain size and Cu(111) intensities.

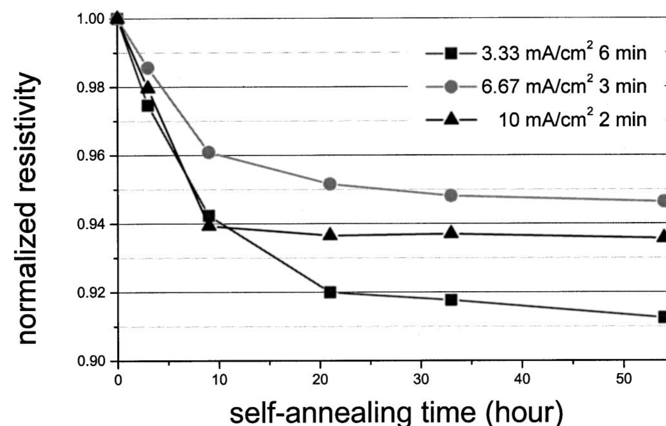

Figure 6. Resistance transients of the films deposited at an equal number of coulombs by the additive-free electrolyte.

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

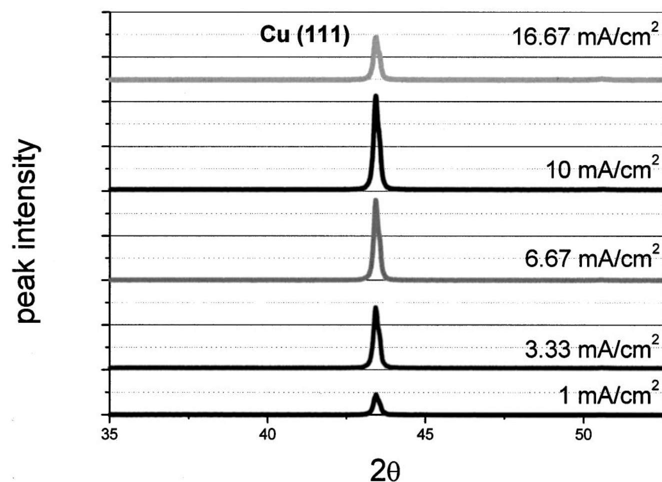

Figure 7. XRD analyses show the textures of deposits vary with plating current densities.

adequate increase of plating current with sufficient polarization enhances Cu (111) intensities. However, when more current is supplied, the less dense packing deposits reduce the (111) peaks. The texture evolutions of Cu films with an increase of plating current densities were consistent with previous discussions on resistivity and surface morphology. Therefore, we suggest that the textures of deposits also correspond to polarization effects.

Conclusions

We investigated the microstructure evolution of the electroplated copper with different plating current densities and found that there were two mechanisms competing with each other to determine the resistivity drop by self-annealing. One is the defects of less dense packing deposits and the other is the underlying energy of the fine-grained deposits. The intensities of Cu(111) peaks increased with an increase of plating current densities, then decreased when more current was supplied. The texture evolution of Cu films with plating current densities is consistent with the evolutions of resistivity and surface morphology. Therefore, the texture of deposits may correspond to polarization effects of Cu electroplating.

Acknowledgments

This work was partially sponsored by the National Science Council of the Republic of China under grant no. NSC91-2721-2317-200. Technical support from the National Nano Device Laboratory and Merck-Kanto Advanced Chemical Limited is also acknowledged.

National Nano Device Laboratories assisted in meeting the publication costs of this article.

References

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Dev.*, **42**, 567 (1998).
2. C. Ryu, K. W. Kwon, A. L. S. Loke, V. M. Dubin, R. A. Rahim, G. W. Ray, and S. S. Wong, in *Digest IEEE 1998 Symposium on VLSI Technology*, p. 156, IEEE (1998).
3. M. Cook and T. L. Richards, *J. Inst. Met.*, **70**, 159 (1994).
4. I. V. Timov, K. S. Stoychev, and I. B. Vitanova, *J. Appl. Electrochem.,* **15**, 887 (1985).
5. T. Ritzdorf, L. Graham, S. Jin, C. Mu, and D. B. Fraser, in *Proceedings of the International Interconnect Technology Conference*, p. 166, IEEE, New York (1998).
6. V. M Dubin, G. Morales, C. Ryu, and S. S. Wong, *Mater. Res. Soc. Symp. Proc.*, **505**, 137 (1998).
7. C. Lingk and M. E. Gross, *J. Appl. Phys.*, **84**, 5547 (1998).
8. C. A. Handwerker and J. W. Cahn, *Mater. Res. Soc. Symp. Proc.*, **106**, 127 (1988).
9. H. Lee, S. D. Lopatin, A. F. Marshall, and S. S. Wong, in *Proceedings of the International Interconnect Technology Conference*, p. 236, IEEE (2000).
10. C. H. Hsieh, S. W. Chou, S. L. Shue, C. H. Yu, and M. S. Liang, in *Proceedings of the International Interconnect Technology Conference*, p. 182, IEEE (2000).
11. S. Vaidya and A. K. Sinha, *Thin Solid Films*, **75**, 253 (1981).
12. D. B. Knorr, D. P. Tracy, and K. P. Rodbell, *Appl. Phys. Lett.*, **59**, 3241 (1991).
13. D. N. Lee, *Mater. Res. Soc. Symp. Proc.*, **427**, 167 (1996).
14. D. N. Lee, S. Kang, and J. Yang, *Plat. Surf. Finish.*, **82**, 76 (1995).
15. W. M. Kuschke, A. Kretschmann, R. M. Keller, R. P. Vinci, C. Kaufmann, and E. Arzt, *J. Mater. Res.*, **13**, 2962 (1998).
16. S. H. Brongersma, E. Richard, I. Vervoort, H. Bender, W. Vandervorst, S. Lagrange, G. Beyer, and K. Maex, *J. Appl. Phys.*, **86**, 3642 (1999).
17. J. M. E. Harper, C. Cabral, Jr., P. C. Andricacos, L. Gignac, I. C. Noyan, K. P. Rodbell, and C. K. Hu, *J. Appl. Phys.*, **86**, 2516 (1999).
18. S. C. Chang, J. M. Shieh, K. C. Lin, B. T. Dai, T. C. Wang, C. F. Chen, Y. H. Li, C. P. Lu, and M. S. Feng, *J. Vac. Sci. Technol. B*, **19**, 767 (2001).
19. M. Aroyo, *Plat. Surf. Finish.*, **85**, 69 (1998).
20. H. B. Oldham and J. C. Myland, in *Fundamentals of Electrochemical Science*, Academic Press, New York (1994).

Downloaded on 2014-04-27 to IP 140.113.38.11 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).