Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thin Solid Films 462–463 (2004) 197–201

www.elsevier.com/locate/tsf

Effect of processing parameters on electroless Cu seed layer properties

Y.C. Ee[a], Z. Chen[a,*], L. Chan[b], Alex K.H. See[b], S.B. Law[b], K.C. Tee[b], K.Y. Zeng[c], L. Shen[c]

[a] *School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*
[b] *Chartered Semiconductor Manufacturing, 60 Woodlands Industrial Park D, Street 2, 738406, Singapore*
[c] *Institute of Materials Research & Engineering, 3 Research Link 117602, Singapore*

Abstract

Electroless Cu seed layer is essential for subsequent copper metallization by electroplating for sub-micron wafer technology. This layer is required to provide good step coverage and high uniformity. In the current work, electroless copper was deposited on a TiN surface activated by palladium. The effect of deposition time on the properties of electroless Cu films was reported. It shows that as the deposition time increases, the surface coverage of Cu film on activated TiN is improved and there is a significant reduction in sheet resistance and an increase in grain size of deposited copper film. Of particular interest is that there exists a preferred Cu (111) crystal orientation in the samples subjected to more than as short as 3 min of deposition. A surface roughness (R_{rms}) of ∼ 17 nm has been achieved. The results obtained in current study points out a promising process for laying down thin Cu seed layer.

Keywords: Electroless plating; Copper metallization; Titanium nitride; Activation

1. Introduction

Copper is drawing attention as an alternate material for global interconnect in ULSI circuit because of its low resistivity, high electromigration resistance and good electrical characteristics as compared to the commonly used aluminum-based interconnects. A Cu seed layer is needed for subsequent electroplating of Cu interconnect. Conventionally the Cu seed is deposited by PVD or CVD techniques.

Recently, electroless deposition of copper as a seeding technology, using only a chemical bath, has received considerable attention [1–3]. Electroless deposition possesses several characteristics not shared by other techniques, such as high uniformity, good surface coverage and improved corrosion resistance [4]. The cost of using this approach is significantly lower than PVD and CVD processes.

Although there have been some studies on the electroless Cu properties [5–8], little is reported on the effect of processing parameters on electroless Cu seed layer properties. This paper reports studies on electroless copper properties such as electrical resistivity, crystal orientation, grain size and surface roughness under different deposition time.

2. Experimental details

The substrates used in this study were TiN coated on silicon wafers with 500 nm thick SiO_2. The TiN film was 25 nm in thickness, deposited by a CVD process. The $TiN/SiO_2/Si$ samples went through the standard SC1 and SC2 cleaning process. Catalyzation was carried out by immersing the cleaned wafers into the activating solution (consists of 300 mg/l $PdCl_2$, 30 ml/l HCl, 20 ml/l HF and DI water) for 3 min at room temperature.

After the activation, electroless copper deposition was conducted at temperature of 60 ± 2 °C for various durations. The electroless copper bath consists of 5 g/l copper sulphate ($CuSO_4 \cdot 5H_2O$), 12 g/l ethylene diamine tetraacetic acid (EDTA), 50 mg/l Triton-X-100 and 5 ml/l formaldehyde (HCHO). The pH level was adjusted to 12.8 by the addition of tetra-methyl-ammonium-hydroxide (TMAH).

Field emission scanning electron microscope (FESEM) was used to observe surface coverage and surface morphology of electroless copper film. The electrical resistivity of the as-deposited electroless copper film was measured using the ResMap™ four-point probe system. Atomic force microscope (AFM) was employed to assess the surface roughness of the film. The crystallinity, texture and grain size of the deposited film were determined by the conventional θ–

---

* Corresponding author. Tel.: +65-6790-4256; fax: +65-6790-9081.
E-mail address: aszchen@ntu.edu.sg (Z. Chen).

0040-6090/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2004.05.018

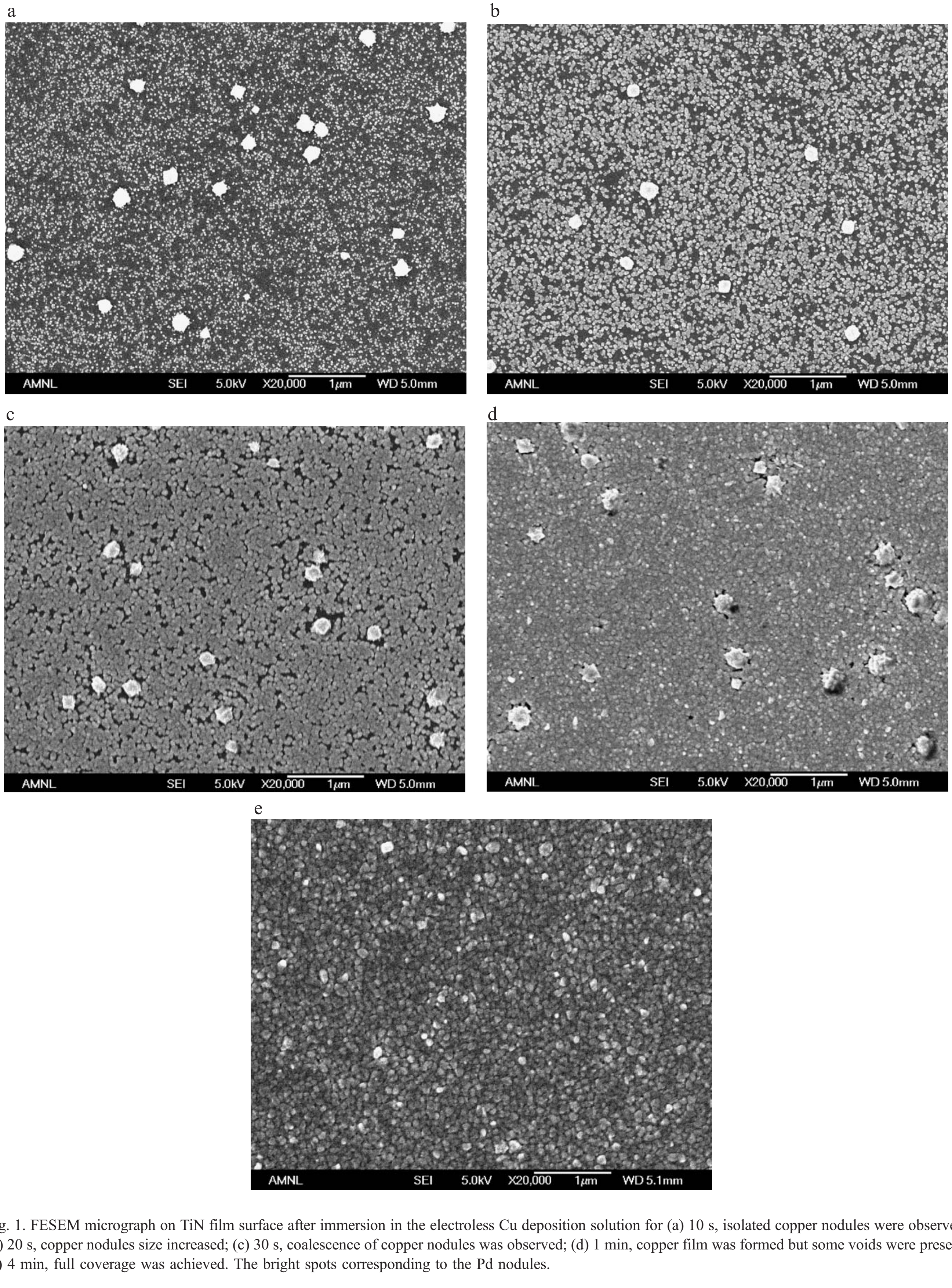

Fig. 1. FESEM micrograph on TiN film surface after immersion in the electroless Cu deposition solution for (a) 10 s, isolated copper nodules were observed; (b) 20 s, copper nodules size increased; (c) 30 s, coalescence of copper nodules was observed; (d) 1 min, copper film was formed but some voids were present; (e) 4 min, full coverage was achieved. The bright spots corresponding to the Pd nodules.

2θ Bragg diffraction method using a Shimadzu™ XRD 6000 diffractometer.

3. Results and discussion

A series of electroless Cu plating experiments revealed that copper plating occurs at very short deposition time. Nevertheless, it still requires some time to achieve a uniform surface coverage on TiN barrier. Pd activated samples were immersed in the bath for 10, 20, 30 s, and 1, 2, 3, 4, 5, 6, 7 and 8 min. Fig. 1a–c show FESEM micrographs on TiN surface after 10, 20 and 30 s immersion in the plating bath, respectively. Initially, isolated copper nodules were observed after 10 s of deposition. The size of these copper nodules increases after 20 s of deposition and coalescence of these copper nodules occurred after 30 s of deposition. When deposition time increased to 1–2 min, an electroless copper film could be clearly observed under FESEM. However, for 1–2 min plating, the coverage was not complete; some voids were clearly seen on the TiN surface as shown in Fig. 1d. Full surface coverage was achieved after 3–4 min plating comparing the FESEM micrographs in Fig. 1d and e. The improvement is due to the growth and coalescence of Cu in between the palladium seeds, forming a more uniform copper film [8]. This study finds that 3–4 min deposition is able to achieve a continuous copper seed layer.

The plating time was also deliberately extended to 30 min in order to test the plating limit of current approach. Delamination of Cu film from the substrate was found at various locations on the surface. The delamination of electroless copper film was believed to be associated with the evolution of hydrogen gas during electroless copper deposition process as indicated in the following equation:

$$\mathrm{Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu^\circ + 2CHOO^- + H_2 + 2H_2O}$$

This is the reaction mechanisms proposed by Bindra and Roldan [9] for formaldehyde oxidation on copper in an alkaline media. It is generally agreed that the atomic hydrogen, H, and molecular hydrogen, H_2, may be incorporated within the deposited materials, which could significantly affect the mechanical properties of the deposited layers. Okinaka and Nakahara [10] suggested that the entrapment of the gas in the film was contained inside the voids under pressure. Such voids in ULSI applications can be of great concern to electromigration reliability of the Cu interconnect. Thus, copper seed layer deposited after long deposition time is not suitable for subsequent electroplating process. We will not discuss results longer than 8 min plating in this paper.

Table 1
Properties of plated Cu film for different plating time

Immersion time in the deposition solution	Measured sheet resistance (Ω/Sq)	Copper grain size (nm)	$I_{(111)}/I_{(200)}$	Copper film surface roughness (RMS)
10 s	113.85	–	–	15.79
20 s	112.66	–	–	17.25
30 s	87.32	24.8	1.15	11.52
1 min	2.00	26.3	1.78	18.41
2 min	0.67	32.5	2.20	17.51
3 min	0.48	31.4	3.28	17.32
4 min	0.40	33.9	3.11	23.42
5 min	0.31	35.1	2.96	27.58
6 min	0.19	37.2	2.97	23.15
7 min	0.15	41.3	3.04	33.37
8 min	0.13	40.2	3.09	27.11

The measured sheet resistance on plated TiN surface is reported in Table 1. There was a sudden drop in sheet resistance from 113.85 to 2.00 Ω/Sq as the plating time increased from 10 s to 1 min. For deposition time under 1 min, the resistance mainly comes from TiN and after 1 min plating, it is dominated by Cu film. The results corroborate our FESEM observation that there is practically no complete coverage of Cu for less than 1 min of plating.

The texture of electroless copper is important as the Cu film is used as seed layer for Cu electroplating in ULSI. The plated Cu film will adopt the crystal orientation of the seed layer (epitaxial effect) and a highly (111) texture is preferred for better electromigration performance [11]. In addition, Cu (111) planes have the lowest interfacial energy among all Cu planes. A preferred crystal orientation of (111) for the samples that have undergone more than 3 min deposition was evidenced by the XRD results as shown in Fig. 2. However, for deposition time less than 3 min, randomly oriented copper grains were obtained. The $I_{(111)}/I_{(200)}$ intensity ratio for 10 and 20 s deposition cannot be obtained due to insignificant amount of copper deposited on TiN, which is under the XRD detection limit. For randomly oriented powdered Cu samples, $I_{(111)}/I_{(200)} = 2.17$. This factor increased to 3.28 as deposition time increased to 3 min. Beyond 3 min plating, the $I_{(111)}/I_{(200)}$ ratio maintained around 3.00. It is noticed that 3 min is the critical time that a continuously dense Cu film starts forming. This work shows that before a dense film is formed, the orientation of Cu grains is probably either random or preferred (100), the diffraction intensity on films below 2 min is too low to reach a solid conclusion (Fig. 2). However, it is evident that once a dense film is formed, the (111) texture quickly establishes.

It is well known that intrinsic stress could be created by the coalescence of neighboring grains [12]. The formation of a texture is a result of minimization of total energy in the film, which consists of surface energy and strain energy. It is not the purpose of this paper to provide a quantitative explanation for the formation of the (111) texture. Nevertheless, a qualitative interpretation is given here. Cu is a highly anisotropic material. The surface energy on (100) plane is higher than (111) plane, while the in-plane elasticity modulus of (100) plane is lower than the one of (111) plane.

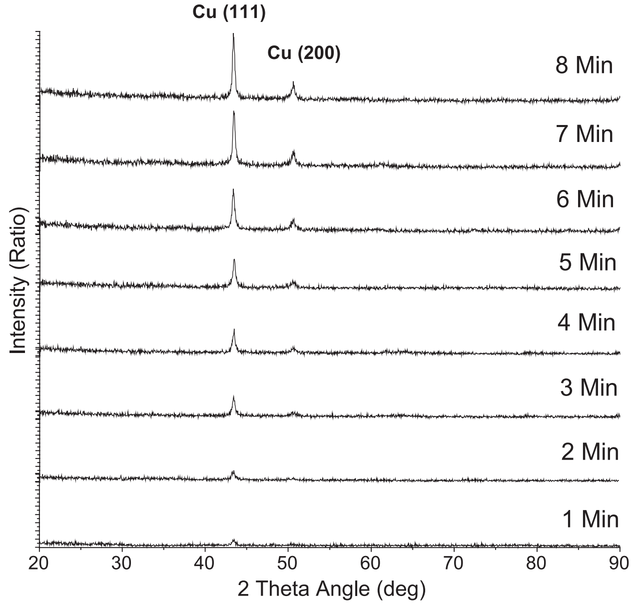

Fig. 2. XRD measurement of electroless copper film for different deposition time. Cu (111) texture was observed after 3 min plating.

While the film is thin, the elastic strain energy component is relatively small compared with the surface energy component, (111) plane is preferred. When the film grows in thickness, there will be a point that total energy is lower with (100) plane. This is because that the strain energy (per unit area) scales with film thickness while the surface energy (per unit area) remains constant. Apparently this transition point also depends on the magnitude of stress, which requires further investigation. The Cu film in current work is very thin (850 Å for 8 min plating) and typically the intrinsic stress for electroless plating is lower than that of eletrolytic plating or one by PVD process, all these factors favor (111) texture in the Cu seed film.

The (111) texture affects the mechanical properties of the Cu film. One of the properties affected is the yield strength since (111) is the slip plane of FCC metal and the Schmid factor for the plane is zero. Therefore a (111) texture is beneficial as far as the strength of the film is concerned.

The mean grain size, d_{mean}, of electroless Cu was estimated from the XRD patterns by using the (111) peak according to Scherrer's equation [13]:

$$d_{\text{mean}} = \frac{0.94\lambda_{\text{Cu}}}{W_{\text{eff}}\cos 2\theta} \qquad (1)$$

where λ_{Cu} is the wavelength of Cu Kα (0.1542 nm), W_{eff} the effective full width at half maximum, and 2θ is the diffraction angle. The results, incorporated in Table 1 and plotted in Fig. 3, show that electroless copper grain size increases almost linearly from 25 to 40 nm as deposition time increases from 30 s to 8 min.

Fig. 4 shows a typical AFM picture of the plated Cu surface. When the plating time increased, there was an increased in surface roughness (Table 1). This is due to the fast catalytic oxidation of formaldehyde on the Cu that was initially deposited on the Pd nodules [14]. An optimum root mean square (RMS) surface roughness of ~ 17 nm has been obtained in the current work for ~ 3 min plating. High uniformity in the seed layer is very important for the following electrolytic Cu plating. The electric field is high at the sharp edges (peaks) of rough films, leading to rapid plating at those regions. After electrolytic plating, the initially non-uniform film becomes even rougher. In the worst scenario voids may form in the recessed areas under such circumstances [5]. Therefore a thin but continuous layer of low roughness and good conductivity is required. Various RMS values between 10 and 50 nm by electroless Cu plating have been reported [5,6,14,15]. The current work has achieved ~ 20 nm RMS by plating for 3–4 min.

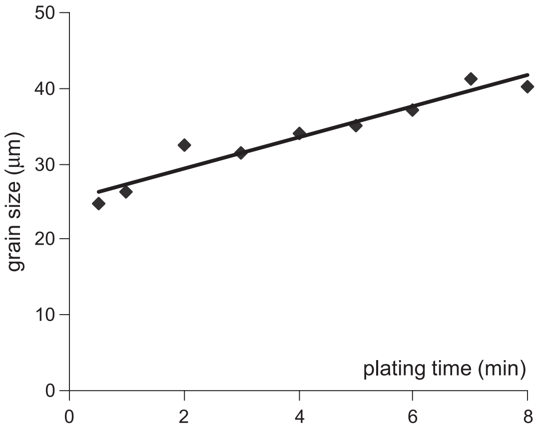

Fig. 3. Grain size increases linearly with plating time.

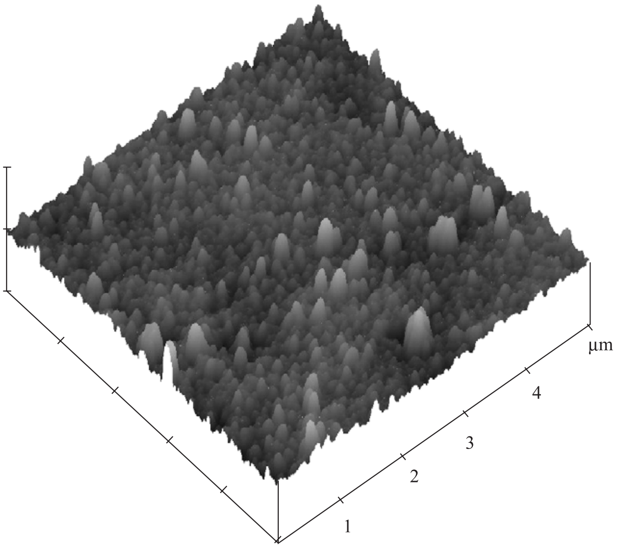

Fig. 4. 3-D stereographical AFM images (5 × 5 μm scan area) of electroless copper on activated TiN after 3 min of deposition. A RMS value of 17 nm was obtained.

4. Conclusion

Electroless Cu deposition provides very good surface coverage in producing a few hundred Å seed layer with high uniformity. From this study, it was determined that the best deposition time is 3–4 min. As the deposition time increases, there is a significant reduction in sheet resistance and an increase in grain size. XRD results show that there exists a preferred (111) crystal orientation in the samples after more than 3 min plating. A surface roughness (R_{rms}) of ~ 17 nm has been achieved. The results obtained in current study points out a promising process for laying down thin Cu seed layer.

References

[1] P.L. Pai, C.H. Ting, IEEE Electron Device Lett. 10 (1989) 423.
[2] J.P. O'Kelly, K.F. Mongey, Y. Gobil, J. Torres, P.V. Kelly, G.M. Crean, Microelectron. Eng. 50 (2000) 473.
[3] Y. Lantasov, R. Palmans, K. Maex, Microelectron. Eng. 50 (2000) 441.
[4] J.L. Vossen, W. Kern, Thin Film Processes, Academic Press, New York, 1978.
[5] W.L. Goh, K.T. Tan, M.S. Tse, K.Y. Liu, Int. J. Mod. Phys. B 16 (2002) 197.
[6] J.C. Patterson, C. Ni Dheasuna, J. Barrett, T.R. Spalding, M. O'Reilly, X. Jiang, G.M. Crean, Appl. Surf. Sci. 91 (1995) 124.
[7] J.C. Patterson, M. O'Reilly, G.M. Crean, J. Barrett, Microelectron. Eng. 33 (1997) 65.
[8] Y.Y. Shacham-Diamand, Electrochem. Solid-State Lett. 3 (2000) 279.
[9] P. Bindra, J. Roldan, Ibid 132 (1985) 2581.
[10] Y. Okinaka, S. Nakahara, Ibid 123 (1976) 475.
[11] C. Ryu, K.W. Kwon, A.S.K. Loke, H. Lee, T. Nogami, V. Dubin, R.A. Kavari, G. Ray, S. Wong, IEEE Trans. Electron Devices 46 (1999) 1113.
[12] B.W. Sheldon, K.H.A. Lau, A. Rajamani, J. Appl. Phys. 90 (2001) 5097.
[13] B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley Pub., London, 1978.
[14] H.T. Ng, S.F.Y. Li, L. Chan, F.C. Loh, K.L. Tan, J. Electrochem. Soc. 145 (1998) 3301.
[15] H.H. Hsu, C.C. Hsieh, M.H. Chen, S.J. Lin, J.W. Yeh, J. Electrochem. Soc. 148 (2001) C590.