

Characterization of electrochromic WO₃ thin films fabricated by an RF sputtering method

Yoon-Tae Park^a, Young Kyu Hong^b and Ki-Tae Lee^{a,*}

^aDivision of Advanced Materials Engineering, Chonbuk National University, Jeonbuk 560-756, Korea

^bKorea Printed Electronics Center, Korea Electronics Technology Institute, Jeonbuk 561-844, Korea

WO₃ thin films were fabricated by RF sputtering deposition. The as-deposited thin films showed uniformity and good adhesion to an ITO layer. The deposition rate increased as the applied power was increased during the RF sputtering deposition. While the as-deposited WO₃ thin films deposited in argon gas alone had very low stoichiometry showing a degradation phenomenon during the transmittance measurement, the WO₃ thin film deposited in a mixture of argon and oxygen gases exhibited better cyclability and a faster response time. The WO₃ thin film prepared at 800 W in the gas mixture showed the best performance with a coloration efficiency of 30.2 cm²·C⁻¹ and a coloring response time of 7 s.

Key words: Electrochromic materials, RF sputtering, Tungsten trioxide, Transmittance, Coloration efficiency.

Introduction

Chromism describes the reversible color change of a material due to an external stimulus. This phenomenon occurs when there is an optical transmittance rate change in the visible ray or infrared range. The discoloration of chromic materials by external factors was first observed by Deb in 1969 [1]. Chromism can be classified as electrochromism, photochromism, and thermochromism according to the nature of the external stimulus. Electrochromism is defined as a reversible change of the optical properties under an applied electric field. Electrochromic materials and devices have been extensively investigated because of their applications as smart windows, displays, and variable reflectance materials [2-5]. High performance electrochromic devices (ECDs) should present high optical contrast, good optical memory, and chemical stability to electrochromic cycles.

Tungsten trioxide (WO₃) has been extensively studied as a promising electrochromic material due to its high coloration efficiency and better electrochemical stability compared with other electrochromic materials [5-7]. The most common deposition techniques used to fabricate WO₃ thin films are thermal evaporation, sol-gel coating, electrodeposition, and sputtering [8-11]. Among these, sputtering is well known as a useful technique to fabricate uniform thin films. However, direct current (DC) sputtering is not suitable for the deposition of insulating materials, because the positive

charge on the target surface rejects the ion flux and may stop the sputtering process. By contrast, radio frequency (RF) sources can be coupled through the insulating target to the plasma. Therefore, conducting electrodes are not necessary. The radio frequency is also high enough to maintain the plasma discharge [12, 13]. Thus, we adopted an RF sputtering method for the fabrication of WO₃ thin films, and investigated the effect of the applied power and the ratio of reaction gases on the film morphology and electrochromic properties.

Experimental Procedures

WO₃ thin films were fabricated using an RF sputtering deposition system with a 120 × 550 mm² WO₃ target (> 99.95%). Prior to sputtering, a pre-sputtering process with only argon gas was performed to eliminate contamination on the target. The base pressure was approximately 33.3 μPa. The substrate was held at room temperature during the deposition. The distance between the substrate and the target was 16 mm. The applied power and the two different atmospheric regimes used for depositions are listed in Table 1.

The morphology and thickness of the as-deposited WO₃ thin films were analyzed by field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi). Electrochemical properties were evaluated using 1 M LiClO₄ in propylene carbonate electrolyte with a three-electrode electrochemical cell, wherein Ag/AgCl and Pt wires were employed as reference and counter electrodes, respectively. In-situ transmittance measurement using a He-Ne laser with a 632.8 nm wavelength was performed during chronocoulometry (CC) at 1 V for 180 s. Then, cyclic voltammetry (CV) analysis was

*Corresponding author:
Tel : +82-63-270-2290
Fax: +82-63-270-2386
E-mail: ktleee71@jbnu.ac.kr

Table 1. Deposition conditions of RF sputtering for WO₃ thin film fabrication.

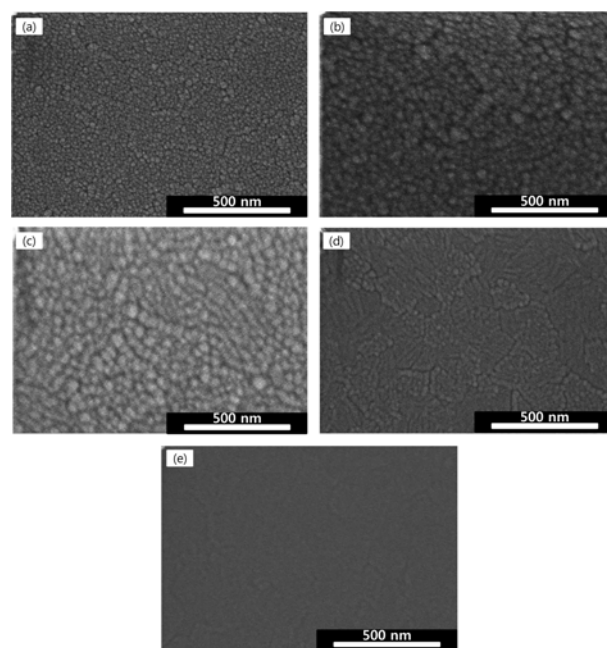
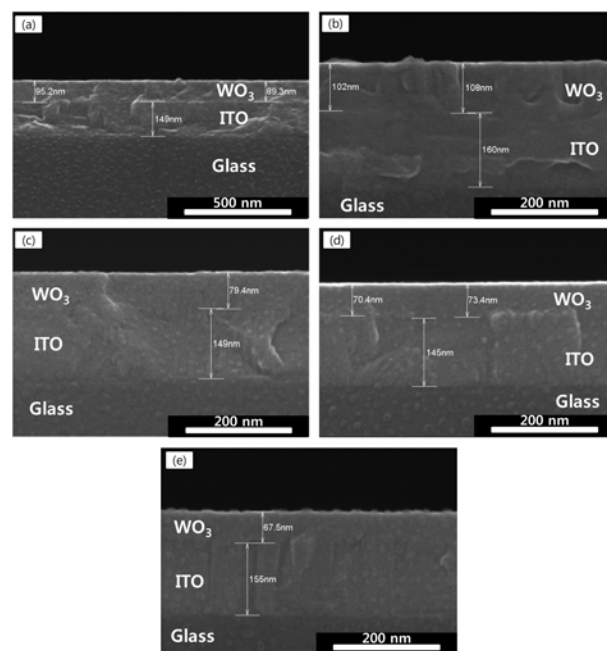
Sample	Power (W)	Gas (sccm)		Scan count
		Ar	O ₂	
P6Ar90	600	90	10	21
P8Ar90	800	90	10	15
P16Ar90	1600	90	10	6
P24Ar90	2400	90	10	2
P8Ar100	800	100	0	4

conducted in a voltage range of +1 to -1 V at a scan rate of 20 mV · s⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was carried out to confirm the electronic structure and stoichiometry of the WO₃ thin films, using an AXIS Nova spectrometer (Kratos Inc.) with an energy resolution of Ag 3d_{5/2} < 0.48 eV.

Results and Discussion

The as-deposited WO₃ thin film morphology was observed by FE-SEM, as shown in Fig. 1. All films were uniformly deposited and the surface morphology of the films depended on the applied power. Although all of the samples had an amorphous phase confirmed by X-ray diffraction, they consisted of surface nano-grains. The grain size has a tendency to increase as the applied power is increased, and the nano-grains formed clusters at a high applied power of 2400 W. Interestingly, the surface morphology was associated with the deposition atmosphere. While the P8Ar90 sample deposited in the gas mixture of argon and oxygen had a rough surface with a granular structure, the P8Ar100 sample deposited in an atmosphere of argon alone had a much smoother surface. This may be due to the relatively larger and heavier oxygen molecules causing the atoms flicked from the target materials to scatter during the sputtering process. Fig. 2 shows the cross-sectional FE-SEM micrographs of the as-deposited WO₃ thin films. All films were fully dense and had good adhesion to the indium tin oxide (ITO) glass. The average thickness of the as-deposited WO₃ thin film and the calculated deposition rates are listed in Table 2. The film thickness could be controlled by the applied power and scan counts. It has been reported that deposition rate and sputtering yield depend on the applied power and working pressure [7, 14]. The deposition rate in this study increased with the applied power. At the same applied power, however, the film deposited in the gas mixture of argon and oxygen showed a much lower deposition rate than that deposited in an atmosphere of argon alone. This may be due to the scattering effect of oxygen molecules, which could reduce the mean free path.

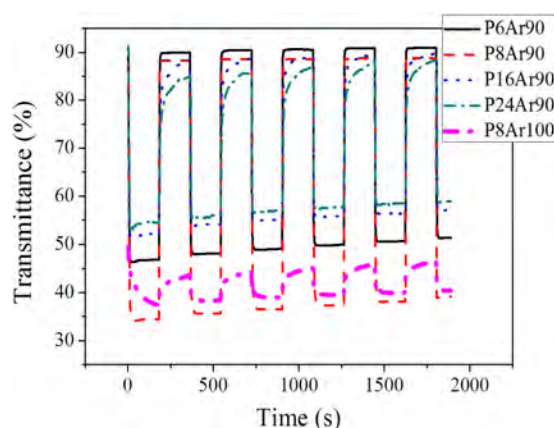
The optical properties of the as-deposited WO₃ thin films are shown in Fig. 3. The colored and the

**Fig. 1.** Surface FE-SEM micrographs of the WO₃ thin films deposited by the RF sputtering method with applied powers of (a) 600 W, (b) 800 W, (c) 1600 W, and (d) 2400 W under a mixture of argon and oxygen gases, and (e) 800 W in argon gas alone.**Fig. 2.** Cross-sectional FE-SEM micrographs of the WO₃ thin films deposited by the RF sputtering method with applied powers of (a) 600 W, (b) 800 W, (c) 1600 W, and (d) 2400 W under a mixture of argon and oxygen gases, and (e) 800 W in argon gas alone.

bleached states of the WO₃ thin films were achieved by reduction at -1 V and oxidation at +1 V vs. Ag/AgCl, respectively. There were no significant differences in transmittance variation with cycles for any of the films. This indicates that the insertion/extraction process by the redox reaction in the as-deposited WO₃ thin films is quite reversible. Based on the data from Fig. 3, the

Table 2. Average thicknesses of the as-deposited WO₃ thin films and the calculated deposition rates under various deposition conditions.

Sample	Thickness (nm)	Deposition rate (nm/scan count)
P6Ar90	92.3	4.4
P8Ar90	105.0	7.0
P16Ar90	79.4	13.2
P24Ar90	71.9	36.0
P8Ar100	67.5	16.9


Fig. 3. Transmittance measurement data of the as-deposited WO₃ thin films fabricated under various sputtering conditions.

calculated transmittance variation (ΔT) for the first cycle is listed in Table 3. The samples deposited at relatively lower power showed large transmittance variations. Comparing the variations in both transmittance variation (Table 3) and film thickness (Table 2), a correlation between transmittance variation and film thickness was detected. The transmittance variation increased with increasing WO₃ thin film thickness. A WO₃ film in a bleached state can be reversed to a colored state by the insertion of both ions and electrons to form tungsten bronze (M_xWO_3) according to the insertion/extraction reaction:



where M^+ denotes H^+ , Li^+ , Na^+ , or K^+ . A thick WO₃ film is able to hold a relatively large amount of lithium. Therefore, the thickest WO₃ film (P8Ar90), as shown in Table 2, showed the largest transmittance variation.

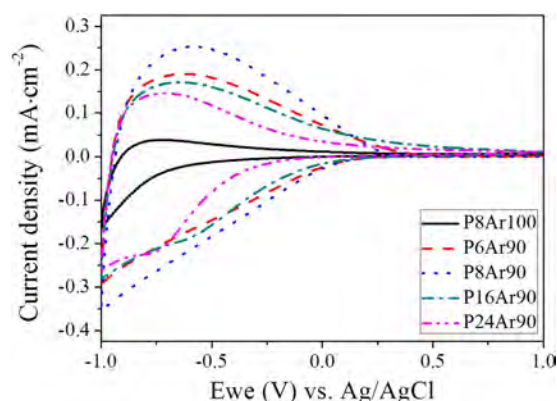
One of important parameters often used to characterize an electrochromic material is its coloration efficiency (CE) as defined by:

$$CE = \frac{\Delta OD}{q/A} = \frac{1}{q/A} \cdot \log \left[\frac{T_{\text{bleached}}(\%)}{T_{\text{colored}}(\%)} \right] \quad (2)$$

where ΔOD is the change in the optical density with charges intercalated per unit electrode area, A is the

Table 3. Electrochromic characteristics of the as-deposited WO₃ thin films.

Sample	$T_{\text{bleached}}(\%)$	$T_{\text{colored}}(\%)$	ΔT	Charge density (mC · cm ⁻²)	Coloration efficiency (cm ² · C ⁻¹)	Response time (s)	
						t_c	t_b
P6Ar90	90.8	50.0	40.8	8.9	29.1	8	5
P8Ar90	88.7	37.4	51.3	12.4	30.2	7	5
P16Ar90	89.4	55.8	33.6	7.1	28.8	8	94
P24Ar90	87.3	57.7	29.6	7.3	24.6	9	95
P8Ar100	45.7	39.6	6.1	3.7	16.8	127	157


Fig. 4. Cyclic voltammogram of the as-deposited WO₃ thin films fabricated under various sputtering conditions.

area of the electrode, q is the electric charge, and T_{bleached} and T_{colored} are the transmittances of the film in the bleached and colored states, respectively. A greater CE means greater transmittance variation per unit charge. The calculated CE values based on the CC data and transmittance data are listed in Table 3. The WO₃ thin film prepared at 800 W in the gas mixture with argon and oxygen showed the best performance, with a coloration efficiency of 30.2 cm² · C⁻¹.

The response time can also be determined using the transmittance data shown in Fig. 3. The response time t_b (or t_c) for bleaching (or coloring) of the WO₃ thin films is defined as the time interval between the highest and lowest variation rates in transmittance. Most of the samples had response times of less than 10 s, except for the P8Ar100 sample deposited in an argon atmosphere. The response time depends strongly on the kinetics of the insertion/extraction reaction of the lithium ions, which is correlated to the stoichiometry and density of the films, and to the number of reaction sites on the surface. As shown in Fig. 1, the P8Ar100 sample deposited in an argon atmosphere had a much smoother surface compared to the other samples. Therefore, the slowest response time observed with the P8Ar100 sample could be due to a lack of reaction sites on its surface. However, in order to explain the slow bleaching response time for the samples deposited at relatively high applied power, further investigations

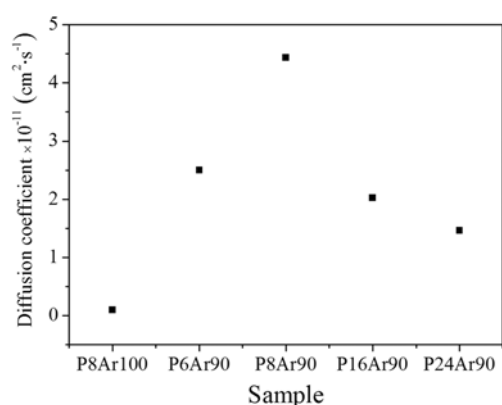


Fig. 5. Variation of the calculated diffusion coefficients of the as-deposited WO_3 thin films.

such as film density measurement or structural analysis should be performed. There may be certain structural changes during extraction or after the insertion of the lithium.

Fig. 4 shows the CV data for the as-deposited WO_3 thin films. The cathodic peak current density is proportional to the capacity of the Li ion insertion. Namely, a higher cathodic peak current density means that more lithium ions have been inserted. Meanwhile, the number of sites where lithium ions can be inserted may have increased as the film thickness increased. The variations in the cathodic peak current density for the as-deposited films corresponded to those of the electrochromic performance parameters, such as ΔT and coloration efficiency, listed in Table 3.

Since the current peak value for each reaction obtained from the CV provides information about the diffusion coefficient of the ion in the electrolyte, the diffusion coefficient of the lithium ion in the WO_3 thin film was calculated using the absolute current density from Fig. 4.

The relationship between the peak current density, i_p , and diffusion coefficient, D , is described in Eq. (3) using the Randles-Sevcik equation [15]:

$$i_p = 2.72 \times 10^5 \times n^{3/2} \times D^{1/2} \times C_0 \times v^{1/2} \quad (3)$$

where n is the number of electrons, D is the diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), C_0 is the concentration of active ions in the solution ($\text{mol} \cdot \text{cm}^{-3}$), and v is the rate at which the potential is swept ($\text{V} \cdot \text{s}^{-1}$). Fig. 5 shows the variations in the calculated diffusion coefficient with various deposition conditions during the RF sputtering process. The diffusion coefficient values are comparable to the values of $2.8 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ reported by Ho et al. [16] and $\sim 10^{-12} \text{ cm}^2 \cdot \text{s}^{-1}$ reported by Xu et al. [17]. The samples deposited at lower applied power showed higher diffusion coefficients. The applied power and atmosphere during the RF sputtering process could affect the as-deposited WO_3 thin film microstructures, such as the surface morphology,

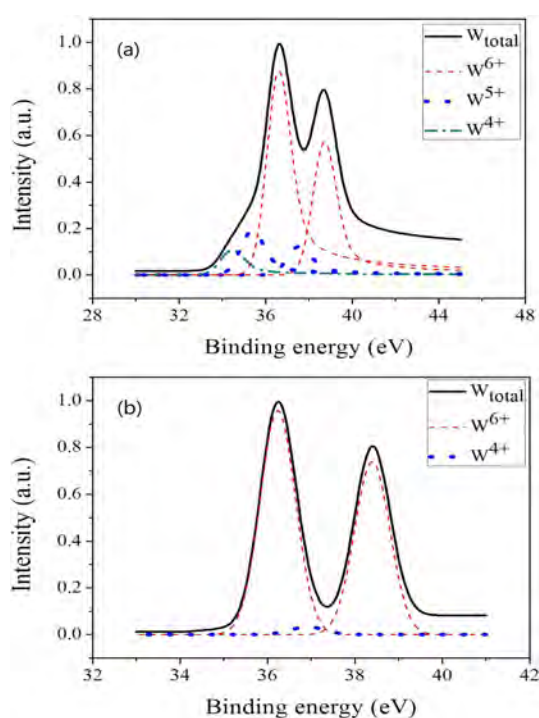


Fig. 6. W 4f core-level spectra of the as-deposited WO_3 thin films fabricated (a) in only argon gas (P8Ar100) and (b) in an argon and oxygen gas mixture (P8Ar90).

Table 4. Composition area, atomic concentration, and oxygen stoichiometry calculated from XPS data.

Sample	Composition area (%)			Atomic concentration (%)		Oxygen stoichiometry (3- δ)
	W ⁶⁺	W ⁵⁺	W ⁴⁺	W	O	
P8Ar100	77.1	16.5	6.4	25.65	65.98	2.57
P8Ar90	97.5	-	2.5	18.92	55.68	2.94

thickness, and density, as shown in Fig. 1 and Table 2. The diffusion coefficient of lithium ions in WO_3 films increased from 3×10^{-12} to $1.5 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ as the density decreased from 5.84 to $3.38 \text{ g} \cdot \text{cm}^{-3}$ [15]. Thus, the density of the as-deposited WO_3 thin films prepared by the RF sputtering process may increase with the applied power. However, further studies to confirm the film density should be performed.

Meanwhile, the sample (P8Ar100) fabricated in an atmosphere of argon alone had a less favorable electrochromic performance than the sample (P8Ar90) deposited in the gas mixture of argon and oxygen, as shown in Figures 3 and 4 and Table 3. This could be attributed to the surface morphology and film density of P8Ar100 leading to a lack of reaction sites and suppression of lithium diffusion, respectively, as discussed. However, despite considering these physical properties, the ΔT value of the P8Ar100 sample was still too low compared to that of the P8Ar90 sample. Moreover, while most of the samples showed over 87% transmittance in the initial state (T_{bleached}), the P8Ar100

sample had only 50% transmittance. XPS analysis was carried out to address this phenomenon. The W 4f core level spectra consisting of the well-resolved spin orbit split doublet peaks corresponding to the W 4f_{5/2} and W 4f_{7/2} states are shown in Fig. 6. Fitting results based on the XPS data in Fig. 6 are also listed in Table 4. In general, transparent WO₃ thin films should have only W⁶⁺. However, the as-deposited WO₃ thin films had W⁶⁺, W⁵⁺, and W⁴⁺ peaks in their XPS spectra, indicating that oxygen non-stoichiometry in WO₃ exists. Interestingly, while the sample fabricated in the all argon atmosphere (P8Ar100) had the oxidation states of W⁶⁺, W⁵⁺, and W⁴⁺, the sample fabricated in the gas mixture of argon and oxygen (P8Ar90) had states W⁶⁺ and W⁴⁺. This indicates that the P8Ar100 sample had a large amount of oxygen vacancies. It has been reported that the color of WO₃ depends on its stoichiometry [18]. While WO₃ with an oxygen stoichiometry over 2.5 is transparent, a blue color appears with an oxygen stoichiometry around or less than 2.5 [19]. The P8Ar100 sample with the lower oxygen stoichiometry around 2.5, as listed in Table 4, showed a blue color in the as-deposited state. Consequently, this led to a lower transmittance value even in its initial state. Moreover, a large amount of oxygen vacancies may hinder the diffusion of lithium ions, which also causes the degradation of electrochromic performance.

Conclusions

WO₃ thin films were deposited using an RF sputtering method at different powers and under different gas atmospheres. The films deposited at lower applied powers exhibited higher coloration efficiencies and shorter response times, indicating the easy transport of ions across the film and an increase in the diffusion coefficient. Meanwhile, the deposition atmosphere during RF sputtering strongly affected the electrochromic properties of the WO₃ thin films, which are correlated with oxygen stoichiometry. The oxidation states of W⁴⁺, W⁵⁺, and W⁶⁺ in the as-deposited WO₃ thin film led to a decrease in transparency, and a large

amount of oxygen vacancies also interrupted the lithium ion diffusion, consequently degrading electrochromic performance.

Acknowledgments

This research was financially supported by the Ministry of Knowledge Economy and Korea Institute for Advancement of Technology through the Research and Development Project for Regional Industry.

References

1. S.K. Deb, Appl. Opt. Suppl. 3 (1969) 192-195.
2. C.G. Granqvist, A. Azens, A. Hjelm, L. Kullman, G.A. Niklasson, D. Ronnow, M.S. Mattsson, M. Veszelei, G. Vaivars, Sol. Energy 63 (1998) 199-216.
3. C.G. Granqvist, P.C. Lansaker, N.R. Mlyuka, G.A. Niklasson, E. Avendano, Sol. Energ. Mat. Sol. C. 93 (2009) 2032-2039.
4. A. Georg, A. Georg, Sol. Energ. Mat. Sol. C. 93 (2009) 1329-1337.
5. R. Baetens, B.P. Jelle, A. Gustavsen, Sol. Energ. Mat. Sol. C. 94 (2010) 87-105.
6. K.K. Purushothanman, G. Muralidharan, J. Sol-gel Sci. Techn. 46 (2008) 190-194.
7. S.J. Yoo, J.W. Lim, Y.E. Sung, Sol. Energ. Mat. Sol. C. 90 (2006) 477-484.
8. M.C. Rao, O.M. Hussain, Res. J. Chem. Sci. 1 [7] (2011) 92-95.
9. J. Livage, D. Ganguli, Sol. Energ. Mat. Sol. C. 68 (2001) 365-381.
10. M. Deepa, M. Kar, D.P. Singh, A.K. Srivastava, S. Ahmad, Sol. Energ. Mat. Sol. C. 92 (2008) 170-178.
11. H. Kawasaki, T. Matsunaga, W. Guan, T. Ohshima, Y. Yagyu, Y. Suda, J. Plasma Fusion Res. 8 (2009) 1431-1434.
12. A. Billard, C. Frantz, J. Phys. III France 6 (1996) 1181-1187.
13. B. Probyn, Vacuum 18 (1968) 253-257.
14. R. Hurditch, Electrocomp. Sci. Tech. 3 (1977) 247-251.
15. M. Deepa, A.K. Srivastava, T.K. Saxena, S.A. Agnihotry, Appl. Surf. Sci. 252 (2005) 1568-1580.
16. C. Ho, I.D. Raistrick, R.A. Huggins, J. Electrochem. Soc. 127 (1980) 343-350.
17. G. Xu, L. Chen, Solid State Ionics 28-30 (1988) 1726-1728.
18. C.G. Granqvist, Appl. Phys. A57 (1993) 3-12.
19. J.G. Zhang, D.K. Benson, C.E. Tracy, S.K. Deb, A.W. Czanderan, J. Electrochem. Soc. 144 (1997) 2022-2026.