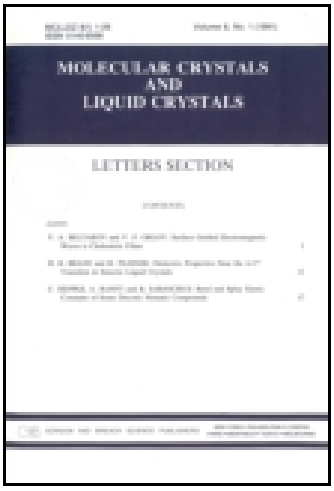

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Thickness Dependence of WO_{3-x} Thin Films for Electrochromic Device Application

Min Hong Kim[a], Hyung Wook Choi[a] & Kyung Hwan Kim[a]
[a] Department of Electrical Engineering, Gachon University, Seongnam, Gyeonggi, Korea
Published online: 17 Nov 2014.

To cite this article: Min Hong Kim, Hyung Wook Choi & Kyung Hwan Kim (2014) Thickness Dependence of WO_{3-x} Thin Films for Electrochromic Device Application, Molecular Crystals and Liquid Crystals, 598:1, 54-61, DOI: 10.1080/15421406.2014.933298

To link to this article: http://dx.doi.org/10.1080/15421406.2014.933298

Mol. Cryst. Liq. Cryst., Vol. 598: pp. 54–61, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.933298

Taylor & Francis
Taylor & Francis Group

Thickness Dependence of WO_{3-x} Thin Films for Electrochromic Device Application

MIN HONG KIM, HYUNG WOOK CHOI, AND KYUNG HWAN KIM*

Department of Electrical Engineering, Gachon University, Seongnam, Gyeonggi, Korea

The phenomenon of color change in a particular material caused by an electrochemical reaction is called "electrochromism." Since the discovery of the electrochromic phenomenon in tungsten oxide, amorphous WO_3 is the most widely studied electrochromic material. Until now, WO_3 remains the most promising candidate for electrochromic devices. Electrochromic devices can switch between two optical states (colored/bleached) by injection/extraction of ions and electrons, based on the modification of transmittance and reflectance that are induced by an applied external voltage. In this study, tungsten oxide (WO_{3-x}) thin films were deposited onto an ITO-coated glass substrate by reactive facing-target sputtering, and their electrochromic properties studied as a function of film thickness. The X-ray diffraction patterns reveal the amorphous properties of all the WO_{3-x} thin films prepared in this study. Of all the different samples prepared in this study, WO_{3-x} thin film of thickness 500 nm exhibited the maximum coloration efficiency of 37.3 cm^2/C.

Kyewords Electrochromic; facing target sputtering; tungsten oxide

Introduction

Electrochromism is defined as a reversible and persistent change in the optical properties of an electroactive material, induced by an applied external voltage [1]. During the last few decades, electrochromic materials have been intensively studied in the field of basic and applied research.

In particular, electrochromic devices have been investigated for their potential applications in energy efficient buildings, non-luminous displays, variable reflectance mirrors, rearview mirrors in automobiles, smart windows, and aerospace industry, wherein they are utilized as energy saving features as a function of radiant heat and radiation [2–4].

Therefore, a combination of display properties and the energy saving properties can result in the implementation of high-performance smart windows. So far, various transition metal oxides are known to show electrochromic properties, in which electrochromism is caused by the double injection/extraction of electrons and ions [5]. Accordingly, based on the nature of ion transfer, electrochromic materials can be divided as cathodic (color

*Address correspondence to Prof. K. H. Kim, Department of Electrical Engineering, Gachon University, Seongnamdearo 1342, Bokjeong, Sujeong, Seongnam, Gyeonggi 461-701, Korea (ROK). Tel.: (+82)31-750-5491; Fax: (+82)31-750-5491. E-mail: khkim@gachon.ac.kr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

upon ion injection) and anodic (color upon ion extraction). Among the various transition metal oxides, tungsten oxide (WO_3) is reported to show outstanding electrochromic performance. For this reason it has received considerable attention among researchers as the most promising candidate for electrochromic devices. In principle, the electrochromic properties of WO_3 thin films are influenced by its microstructure, chemical composition, and the synthesis process [6]. Thus far, WO_3 thin films have been prepared using various synthesis processes, including sputtering [7], pulsed laser deposition [8], sol–gel synthesis [9], electrophoretic deposition (EPD) [10], thermal evaporation [11], chemical vapor deposition [12], and electron-beam evaporation [13]. We using facing-target sputtering (FTS) offers many advantages, such as low working pressure and low temperature [14]. Therefore, in this study, WO_3 thin films are deposited by using facing-target sputtering in mixed argon and oxygen atmosphere. The significant parameter in a sputtering process is the thickness of the thin film. Hence, we have investigated the correlation between the electrochromic properties and thickness of tungsten oxide thin films, with an aim to find the optimum thickness with superior electrochromic properties.

Experimental

Deposition of WO_{3-x} Thin Films

Fig. 1 shows the FTS equipment used for the deposition of tungsten oxide thin films. In conventional sputtering methods, the substrate is positioned in such a way that it is exposed to the plasma. This limits the fabrication of high quality thin films because of the damage caused to the thin film surface. However, the FTS system used in this study is designed to array two targets that face each other, to facilitate the fabrication of thin film in a stable sputtering atmosphere. This design also protects the substrate and the thin films from the bombardment of high-energy particles during the sputtering process [14]. The FTS system can suppresses the damage caused to the substrate by high-energy particles,

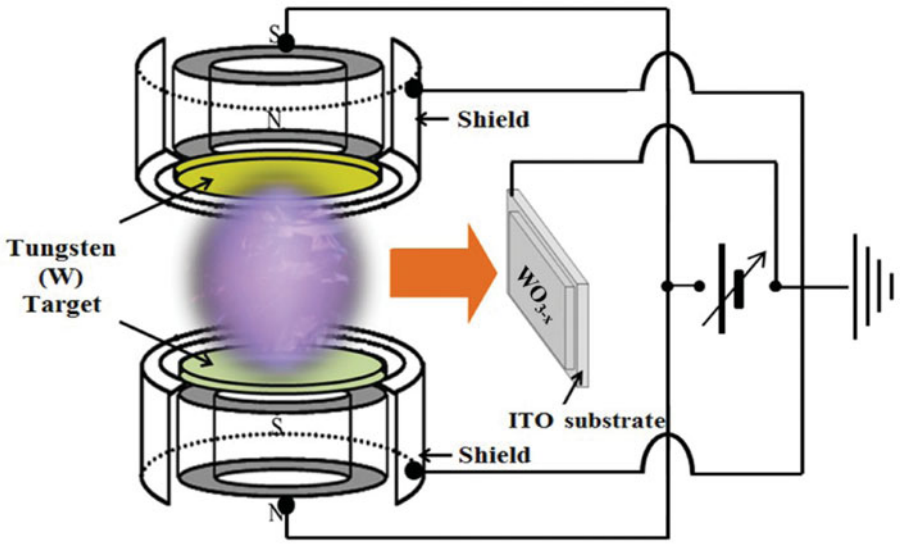

Figure 1. Facing targets sputtering system equipment.

Table 1. Deposition condition of WO_{3-x} thin films

Deposition parameter	Sputtering condition
Target	W(pure 99.95%)
Substrate	ITO coated Glass
Power density	4 W/cm^2
Backgroud pressure	2.6×10^{-4} Pa
Working pressure	0.13 Pa
O_2 gas flow ratio [O_2/Ar + O_2]	0.7
Thickness	100, 300, 500, 800, 1100 nm
Substrate temperature	R.T

such as electrons and partial ions. For these reasons, the FTS system is considered one of the most attractive techniques for the fabrication of high quality thin films. The tungsten oxide thin films were deposited onto an indium tin oxide (ITO)-coated glass substrate, from W metal target (99.95% purity, 2 in. LTS) at room temperature, by using reactive FTS in an argon and oxygen plasma. Before film deposition, the ITO coated glass substrate was ultrasonically cleaned, first with acetone for 20 min, then with distilled water for 15 min, and finally with ethanol for 20 min. The cleaned substrates were then dried in a stream of N_2 gas. Before introducing the gases, the sputtering chamber was evacuated to 2.4×10^{-4} Pa using a turbo molecular pump. Prior to deposition, the target was sputtered for 30 min to clean the surface of any oxide layer. The oxygen flow ratiowas adjusted to a constant value of $[O_2/(Ar+O_2)]$ratio of 0.7 by using mass-flow controllers. Table 1 summarizes the parameters adopted for the sputter deposition of WO_{3-x} thin films.

Characterization

The thickness of the deposited WO_{3-x} thin films was measured by using a surface profiler (alpha step), and the crystal structure was investigated by using X-ray diffraction (XRD, Rigaku, D/MAX-2200) with Cu-Ka radiation (λ =1.5418 Å) X-ray source at 40 kV and 20 mA in the scanning angle (2θ) from 20° to 80°. The optical properties were measured by using a UV-Vis spectrometer (lambda 750, PerkinElmer, USA). Furthermore, the electrochromic properties of the deposited WO_{3-x} thin films were measured by using cyclic voltammetry (VSP-CHAS potentiostat), which was performed using a three-electrode system composed of WO_{3-x} as the working electrode, Ag/AgCl (3M NaCl) as the reference electrode, and Pt wire as the counter electrode. The electrolyte was composed of 0.1M $LiClO_4$–propylene carbonate solution. The measurements were performed at a scan rate of 30 mV/s in the potential range of −1.5 to 1.5 V.

Results and Discussion

Fig. 2 shows X-ray diffraction patterns of all the WO_{3-x} thin films. Other than the peak of the indium tin oxide, tungsten oxide peaks were not found under any deposition condition. In addition, the diffraction patterns of all the thin films were almost similar, without any significant changes. This indicates the amorphous properties of the WO_{3-x} thin films, which could have resulted from the internal stress [15]. In general, amorphous tungsten oxide thin films exhibit better properties than the crystalline thin films. It is usually a properties of thin films fabricated by sputtering system at room temperature. Therefore, the difference in

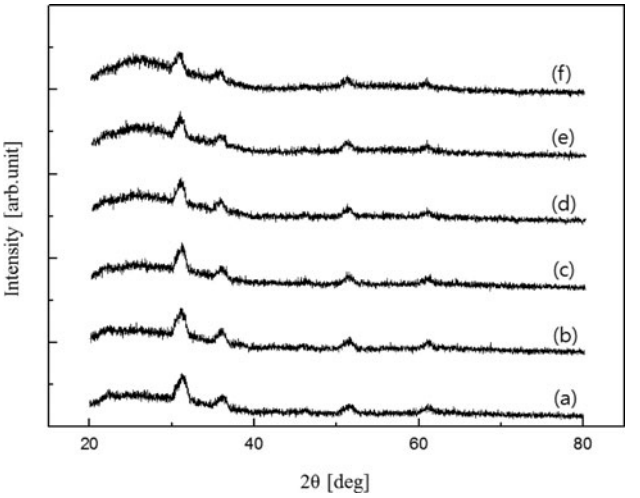

Figure 2. X-ray diffraction patterns of the deposited WO_{3-x} thin films as a function of the thickness: (a) ITO coted glass, (b) 100 nm, (c) 300 nm, (d) 500 nm, (e) 800 nm, and (f) 1100 nm.

the thickness of the thin film did not have any significant effect on the phase. Fig. 3 shows the cyclic voltammograms (CVs) of the WO_{3-x} thin films of different thickness obtained by varying the sputtering conditions. The EC performance of the WO_{3-x} thin films were estimated by recording the CV curves at a scanning rate of 30 mV/s in the voltage range of −1.5 to 1.5 V. It is well known that the coloration and bleaching of the WO_{3-x} thin films are associated with the injection and extraction of Li^+ ions and electrons, which can be determined as [16],

$$WO_{3-x}(\text{bleached}) + xe^- + xLi^+ \leftrightarrow Li_xWO_{3-x}(\text{colored}),$$

where Li^+ is an ion in lithium perchlorate organic solution. Upon application of negative bias, blue color is observed, indicating the injection of Li^+ into the WO_{3-x} thin film. On the

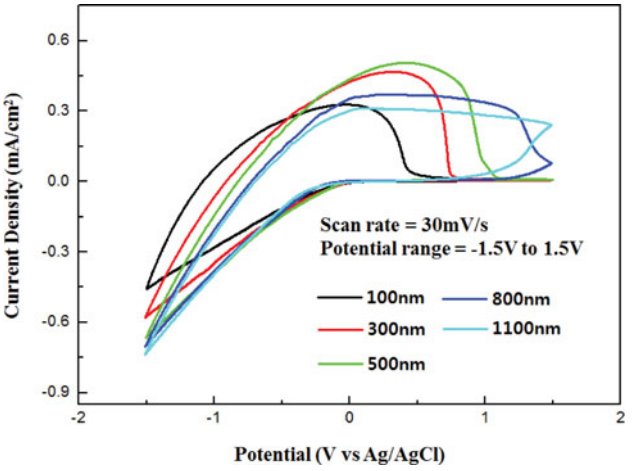

Figure 3. Cyclic voltammograms (CVs) of the deposited WO_{3-x} thin films as a function of the thickness.

other hand, applied positive bias results in bleaching, corresponding to the extraction process. The CV curves of all the thin films were almost similar. However, the cathodic current density was observed to increase continuously with increasing thickness.The increase in anodic and cathodic current with film thickness indicates an increase in the amount of ions and electrons in the thin film. As evidenced from the results, WO_{3-x} thin film of thickness 1100 nm shows a high cathodic current density of 0.74 mA/cm^2 when compared to that of the other WO_{3-x} thin films.

Fig. 4 shows the optical transmittance of WO_{3-x} thin films of thickness 100 nm, 300 nm, 500 nm, 800 nm, and 1100 nm, which indicate as-deposited, colored, and bleached states in the visible range. As shown in the figure, the transmittance of the films varied as a function

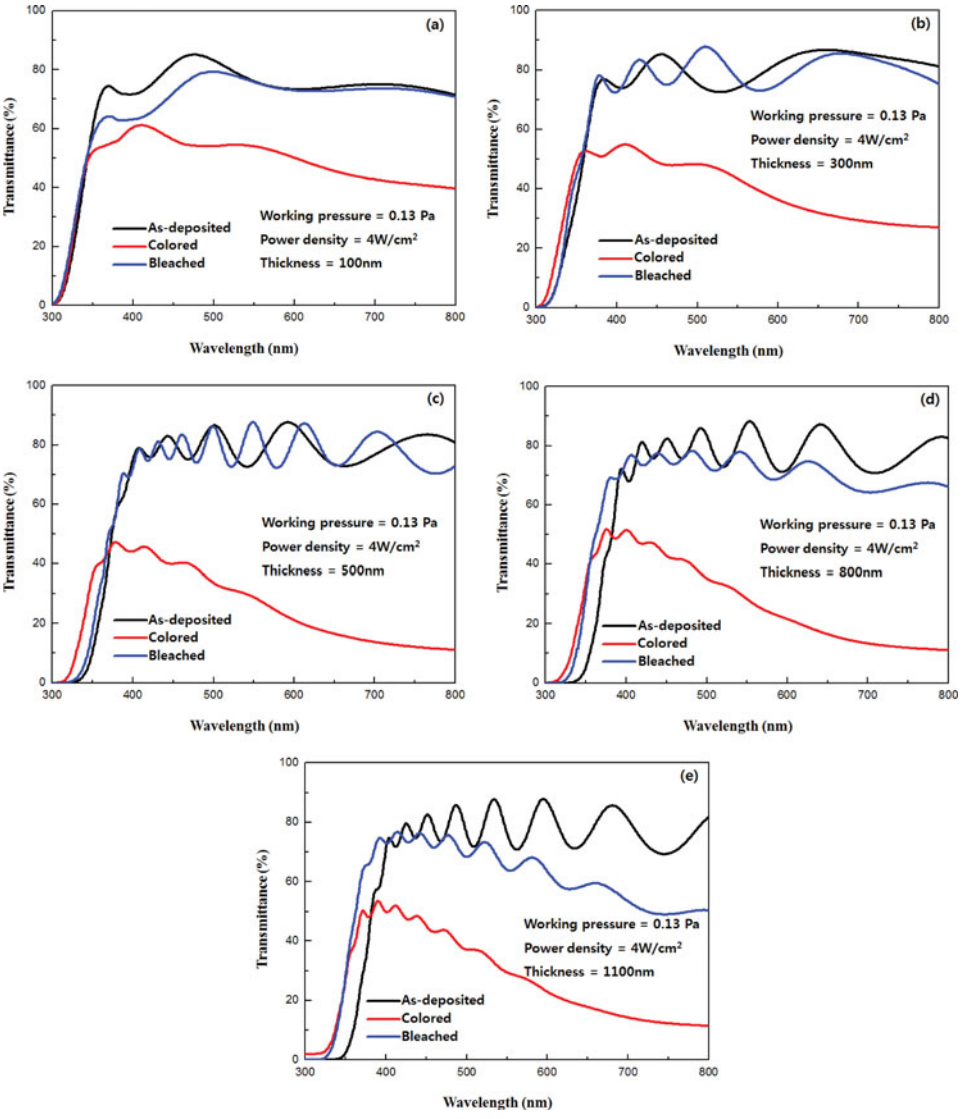

Figure 4. Optical transmittance of WO_{3-x} thin films: (a) 100 nm, (b) 300 nm, (c) 500 nm, (d) 800 nm, and (e) 1100 nm.

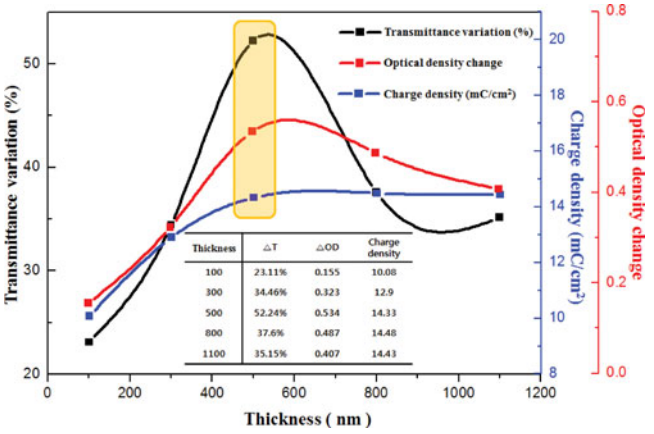

Figure 5. Optical density change (ΔOD), transmittance variation (ΔT), and Charge density (mC/cm^2) of the WO_{3-x} thin films in the visible range.

of thickness. However, regardless of the difference in thickness, all the WO_{3-x} thin films exhibited transparent state without change in the blue color. In general, WO_{3-x} thin films exhibit transparent state at x below 0.3 [17]. The reduction in the transmittance spectra at the wavelength of ~350 nm is due to the fundamental absorption edge, as previously reported in the literature [18]. The transmittance spectra of the WO_{3-x} thin films of different thickness were almost similar. However, the oscillation behavior of the transmittance spectra could be related to the thin film thickness, which arose from optical interference due to the multilayered component [19].

The color of the WO_{3-x} thin films transformed to dark blue upon injection of electrons and Li^+ ions into these thin films. The electrochromic device can change its optical properties with the initiation of an external voltage, and can revert to the original state by reversing the external voltage.

Fig. 5 shows the change in the optical density (ΔOD), the variation in transmittance (ΔT), and Charge density (mC/cm^2) of the WO_{3-x} thin films in the visible range. The variation in transmittance (ΔT) of WO_{3-x} thin films were estimated to be 23.11, 34.46, 52.24, 37.6, and 35.15%, respectively, using the relation

$$\Delta T = T_{bleached} - T_{colored},$$

where $T_{bleached}$ is the transmittance of the thin film in the bleached state and $T_{colored}$ is the transmittance of the thin film in the colored state. The highest value of ΔT was observed in WO_{3-x} thin film of thickness 500 nm. We considered that the decrease in the transmittance of bleached state ($T_{bleached}$) in thin films of thickness above 500 nm is due to the accumulation of large amount of ions and electrons in the WO_{3-x} thin films.

The optical density refers to the light absorbing capability of the electrochromic thin films [20]. The ΔOD value can be determined using the following relation.

$$\Delta OD = \log[T_{bleached}/T_{colored}]$$

The WO_{3-x} thin film of thickness 500 nm was obtained better optical density change properties than the other thin films.

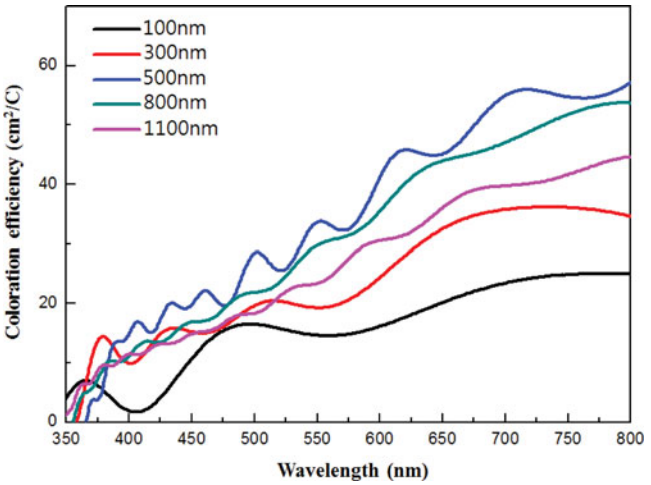

Figure 6. Coloration efficiency (cm^2/C) of the WO_{3-x} thin films in the visible range.

Fig. 6 shows the coloration efficiency (cm^2/C) of the WO_{3-x} thin films in the visible range, which is one of the significant parameters for determining the practical application of an electrochromic device. The coloration efficiency can be determined as,

$$CE = OD/Q$$

where Q is the injected charge per unit area. From the above results, a value of coloration efficiency for 500 nm thicknesses of WO_{3-x} thin film was obtained maximum value about 37.3 cm^2/C. As the film thickness increases, large amount of ions and electrons are injected in the thin films. However, in case of thin films with thickness more than 500 nm, the transmittance value decreases. This could be attributed to the accumulation of Li^+ ions in the WO_{3-x} thin films. Yoshiike reported that Li^+ exists in combined form as W-OLi, which accumulates in the thin film during repeated coloring and bleaching process [21]. Therefore, it is reasonable to consider that the observed decrease in transmittance is caused by structural deformation, which decreases the mobility of the ions during the bleaching process. In addition, the observed decrease in the coloration efficiency of the thin films with thickness above 500 nm is considered to be due to accumulation of Li^+ ions in the WO_{3-x} thin films. The above mentioned results clearly reveal the correlation between the electrochromic properties and thickness of the tungsten oxide thin films.

Conclusions

In this study, electrochromic WO_{3-x} thin films of various thicknesses were deposited by reactive facing-target sputtering at the oxygen flow ratio $[O_2/(Ar+O_2)]$ of 0.7. The XRD pattern of all the WO_{3-x} thin films of various thicknesses indicated amorphous properties, which could be attributed to the internal stress of tungsten oxide films. This is a typical characteristic of thin films fabricated by sputtering at room temperature. Furthermore, the EC performance of the WO_{3-x} thin films was evaluated by recording the CV curves at a scanning rate of 30 mV/s in the potential range between −1.5 and 1.5 V. The CV curves of all WO_{3-x} thin films prepared in this study were almost similar. However, the cathodic current density increased continuously with increase in film thickness. All the WO_{3-x} thin

films observed transparent state without change in the blue color. Generally, WO_{3-x} thin films exhibit transparent at x below 0.3. The oscillation behavior of transmittance spectra can be related to the thickness of the thin film and arise from the optical interference due to the multilayer component. The of WO_{3-x} thin film of 500 nm thickness was obtained better optical density change properties than the other thin films, and coloration efficiency for 500 nm thicknesses of WO_{3-x} thin film was obtained maximum value about 37.3 cm^2/C. Therefore, we are obtained that the correlation between tungsten oxide thin films and electrochromic properties in different thickness.

Acknowledgments

This work was supported by the Human Resources Development Program (NO. 20124030200010) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by Korea government Ministry of Trade, Industry and Energy.

References

[1] Somani, P. R., & Radhakrishnan, S. (2002). *Mater. Chem. Phys.*, *77*, 117.
[2] Granqvist, C. G., Avendano, E., & Azens, A. (2003). *Thin Solid Films*, *442*, 201, 201.
[3] Azens, A., Hjelm, A., Le Bellac, D., Granqvist, C. G., Barczynska, J., Pentjuss, E., Gabrusenoks, J., & Wills, J. M. (1996). *Solid State Ionics*, *86–88*, 943.
[4] Lamper, C. M. (1984). *t Sol. Energy Mater.*, *11*, 1.
[5] Livage, J., & Ganguli, D. (2001). *Sol. Energy Mater. Sol. Cells*, *68*, 365.
[6] Granqvist, C. G., Avendano, E., & Azens, A., (2003). *Thin Solid Films*, *442*, 201–211.
[7] He, J. L., & Chiu, M. C. (2000). *Surf. Coatings Technol.*, *127*, 43.
[8] Ozera, N., & Lampert, M. (1999) *Thin Solid Films*, *349*, 205.
[9] Nishio, K., & Tsuchiya, T. (2001) *Sol. Energy Mater. Sol. Cells*, *68*, 279.
[10] Deepa, M., Kar, M., Singh, D. P., Srivastava, A. K., & Ahmad, S. (2008). *Sol. Energy Mater. Sol. Cells*, *92*, 170.
[11] Porqueras, I., & Bertran, E. (2001). *Thin Solid Films*, *398–399*, 41.
[12] Ivanova, T., Gesheva, K., Hamelmann, F., Popkirov, G., Abrashev, M., Ganchev, M., & Tzvetkova, E. (2004). *Vacuum*, *76*, 195.
[13] Joraid, A. A. (2009). *Curr. Appl. Phys.*, *9*, 73.
[14] Rim, Y. S., Kim, D. H., & Kim, K. H. (2009). *Mol. Cryst. Liq. Cryst.*, *514*, 99–108.
[15] Wang, X. G., Jiang, Y. S., Yang, N. H., Yuan, L., & Pang, S. J. (1999). *Appl. Surf. Sci.*, *143*, 135.
[16] Faughnan, B. W., Crandall, R. S., & Heyman, P. M. (1975). *RCA Rev*, *36*, 177.
[17] Chatten, R., Chadwick, A. V., Rougier, A., & Lindan, P. J. D. (2005). *J. Phys. Chem. B*, *109*, 3146.
[18] Gesheva, K., Szekeres, A., & Ivanova, T. (2003) *Sol. Energy Mater. Sol. Cells*, *76*, 563.
[19] Yang, D., & Xue, L. (2004). *Thin Solid Films*, *469–470*, 54.
[20] Lu, H. H (2008). *J. Alloys Compd.*, *465*, 429.
[21] Yoshiike, N., Mizuno, Y., & Kondo, S. (1984). *J. Electrochem., Soc.*, *131*, 2634.