Journal of the Korean Crystal Growth and Crystal Technology
Vol. 14, No. 4 (2004) 145-150

Structural, electrical and optical properties of Al-doped ZnO thin films by pulsed DC magnetron sputtering

Hyungduk Ko, Choong-Sun Lee, Ki-Chul Kim*, Jae Seok Lee**, Weon-Pil Tai***, Su-Jeong Suh and Young-Sung Kim†

Advanced Material Process of Information Technology, Sungkyunkwan University, Suwon 440-746, Korea
**Information Storage Device, Electronics and Telecommunications Research Institute, Daejeon 305-350, Korea*
***Division of Material Science and Engineering, Korea University, Seoul 130-650, Korea*
****Institute of Advanced Materials, Inha University, Inchon 402-751, Korea*

(Received June 4, 2004)
(Accepted July 29, 2004)

Abstract We have investigated the structural, electrical and optical properties of Al-doped ZnO (AZO) thin films grown on glass substrate by pulsed DC magnetron sputtering as functions of pulse frequency and substrate temperature. A highly c-axis oriented AZO thin film is grown in perpendicular to the substrate when pulse frequency of 30 kHz and substrate temperature of 400°C was applied. Under this optimized growth condition, the resistivity of AZO thin films exhibited 7.40×10^{-4} Ω-cm. This indicated that the decrease of film resistivity resulted from the improvement of film crystallinity. The optical transmittance spectra of the films showed a very high transmittance of 85~90 % in the visible wavelength region and exhibited the absorption edge of about 350 nm. The results show the potential application for transparent conductivity oxide (TCO) thin films.

Key words Pulsed DC magnetron sputter, Al-doped ZnO, Pulse frequency, Substrate temperature, Optical properties

1. Introduction

The transparent and conductive oxide (TCO) thin films have been widely used in various fields as transparent electrode for display device. For these applications, TCO films should have low resistivity (10^{-3}~10^{-4} Ω-cm) and a very good optical transmittance (80~90 %) in visible light range. At present, ITO films have been widely used for photovoltaic devices and flat panel display because of its good electrical and optical properties. However, ITO films require high cost for its preparation and have low stability to H_2 plasma. Recently, Al-doped zinc oxide films (AZO) have attracted much attention for transparent and conductive film material because of a wide band gap, high transparency and low resistivity. Besides AZO thin films have a lot of advantages, such as no toxicity, low cost, and high stability against hydrogen plasma [1-7].

Up to now, several techniques such as r.f. sputtering [8], spray pyrolysis [9], sol-gel [10], pulsed laser deposition (PLD) [11], and chemical vapor deposition (CVD) [12] have been employed for preparing AZO thin films. Among these techniques, the sputtering process is the most promising method for depositing AZO films because it has many advantages of low substrate temperature, good surface flatness, and low cost [13-16]. However, pulsed DC magnetron sputtering process has been seldom tried for the preparation of AZO films in spite of its good capability. Especially, bipolar pulse DC magnetron sputtering process has attracted much attention because it has higher deposition rate than conventional r.f. magnetron sputtering process as well as it can alleviate the main problem associated with the continuous DC sputtering process such as the occurrence of arc events at the target. It also has advantages of low cost and low temperature deposition, compared to MOCVD and PLD process [17-20].

Therefore, in this study, we tried to prepare the good electrical and optical AZO thin films on glass by pulsed DC magnetron sputtering from ZnO : Al target at pure Ar atmosphere. The structural, electrical and optical properties of the AZO films were investigated as function of pulse frequency and substrate temperature.

†Corresponding author
Tel: +82-31-299-6702
Fax: +82-31-290-5644
E-mail: youngsk@skku.edu

2. Experiments

AZO films were deposited on glass by asymmetrical bipolar pulsed DC magnetron sputtering. The sputtering target was fabricated by sintering 99.0 at% ZnO and 1.0 at% Al_2O_3 powder. The sputtering chamber was pumped down to 5×10^{-6} Torr by turbo molecular pump and Ar gas was only used as sputtering gas. ZnO : Al target was pre-sputtered by Ar plasma for 5 min to clean the target. Working pressure was 5 mTorr during every sputtering process. First, the effect of pulse frequency on structural, electrical and optical properties was investigated by varying pulse frequency from 10 to 50 kHz. At the same time, the effect of substrate temperature on structural, electrical and optical properties were studied by varying it from 25°C (room temperature) to 500°C. The thickness of all ZnO films was controlled about 250 nm confirmed by observation of the cross section of the fractured films with a scanning electron microscopy. X-ray diffractometer (XRD) analysis was performed to investigate the crystallographic structure of AZO films. The surface morphologies of films were observed by scanning electron microscopy (SEM). The electrical resistivity of films was investigated by van der Pauw method after depositing Cu electrode on AZO film and the optical transmittance of AZO films were measured by UV-visible spectrometer.

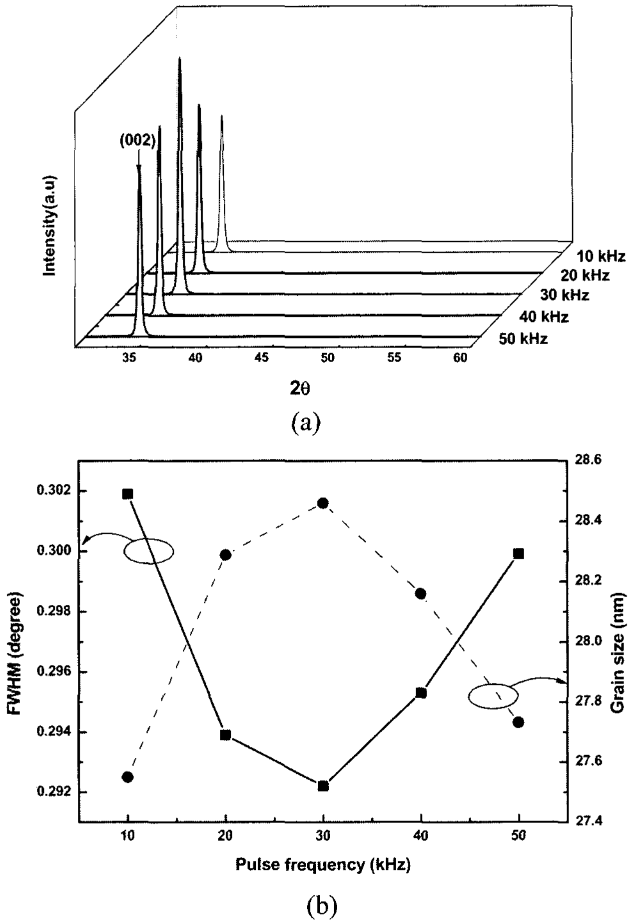


Fig. 1. XRD diffraction patterns (a) and FWHM (b) of AZO films prepared at different pulse frequency on the substrate temperature of 400°C, under 5 mTorr.

3. Results and Discussion

3.1. Structural properties

Figure 1 shows the XRD patterns and full width at half maximum (FWHM) corresponding to (002) peak of AZO films prepared at different pulse frequency. As shown in Fig. 1a, all the films showed highly preferred orientation of (002) plane regardless of the pulse frequency. However, the peak intensity of (002) plane had the highest value when the pulse frequency of 30 kHz was applied to a target. It indicated that a highly c-axis preferred AZO film was grown in perpendicular to the substrate when the pulse frequency of 30 kHz was applied to a target. Figure 1b show the FWHM and grain size of AZO films prepared as a function of pulse frequency. The FWHM of AZO thin films decreased with the increase of pulse frequency from 10 to 30 kHz, and then it increased above the pulse frequency of 40 kHz. Therefore, when the pulse frequency of 30 kHz was applied to a target, the grain size became largest and the crystallinity was improved due to reducing defects in grain boundaries [5].

Figure 2 shows the XRD patterns and FWHM corresponding to (002) plane of AZO films prepared as a function of substrate temperature. As shown in Fig. 2a, the films prepared at low temperatures have a very weak c-axis orientation, however, the films prepared at higher temperatures exhibit a strong c-axis orientation. That is, the peak intensity of (002) plane increased with the increase of substrate temperature from 25°C to 400°C, however, the substrate temperature of 500°C resulted in the decrease of peak intensity. These results indicate that 300~400°C is the suitable deposition temperature for the growth of the (002) oriented AZO thin film on glass substrate. Figure 2b shows the FWHM and grain size of AZO films prepared at different substrate temperature. FWHM decreased with the increase of substrate temperature in the range from 25 to 400°C, even though the increase of the substrate temperature above 400°C resulted in a little increase of FWHM. It can be assumed that the optimized substrate temperature enables the atoms to have enough surface mobility into an effective equilibrium state [17].

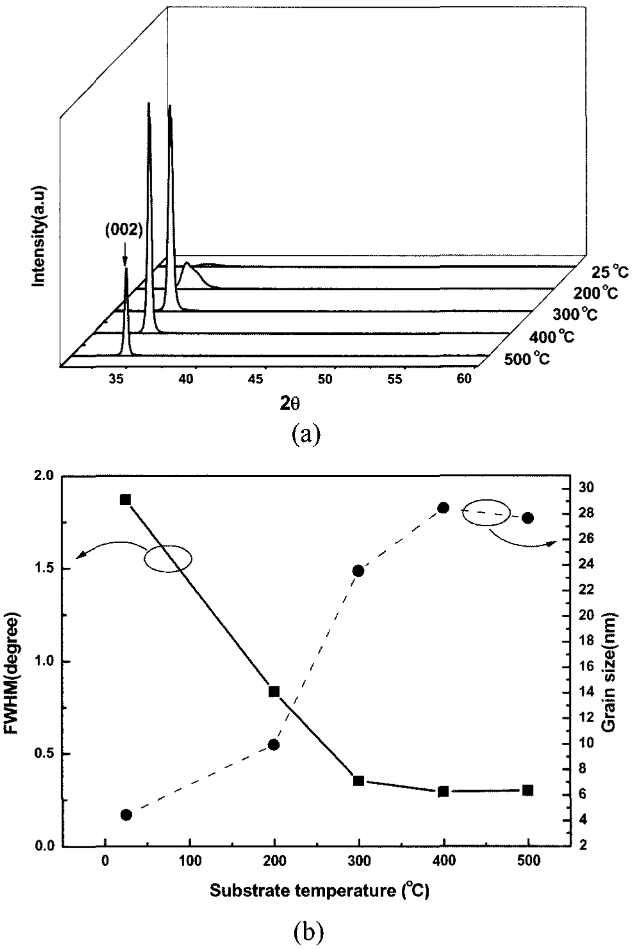


Fig. 2. XRD diffraction patterns (a) and FWHM (b) of AZO films prepared at different substrate temperature on the pulse frequency of 30 kHz, under 5 mTorr.

Figure 3 shows SEM micrograph of AZO films prepared as a function of pulse frequency at a substrate temperature of 400°C. All the films had tightly packed fibrous grain and relatively smooth domed surfaces. However, the smoothest and densest AZO films were grown when pulse frequency of 30 kHz was applied. These results are on a good agreement with Thorntons structure zone model [6]. According to this model, the surface microstructure was classed in term of four zones as function of T/T_m (T : substrate temperature, T_m : ZnO melting point) and Ar gas pressure. Deposition parameters of the films shown in Fig. 3 are T/T_m of 0.27 and Ar pressure of 5 mTorr, which is under that of fibrous structure proposed by Thornton.

3.2. Electrical properties

The electrical properties of AZO films under different deposition condition were measured by van der pauw method. Figure 4a shows the electrical resistivity of AZO films prepared at different pulse frequency. The resistivity of films decreased with increase of pulse frequency from 10 to 30 kHz. However, it increased when higher pulse frequency than 30 kHz was applied. These results were consistent with the results of c-axis preferred orientation and crystallinity shown in Fig. 1. That

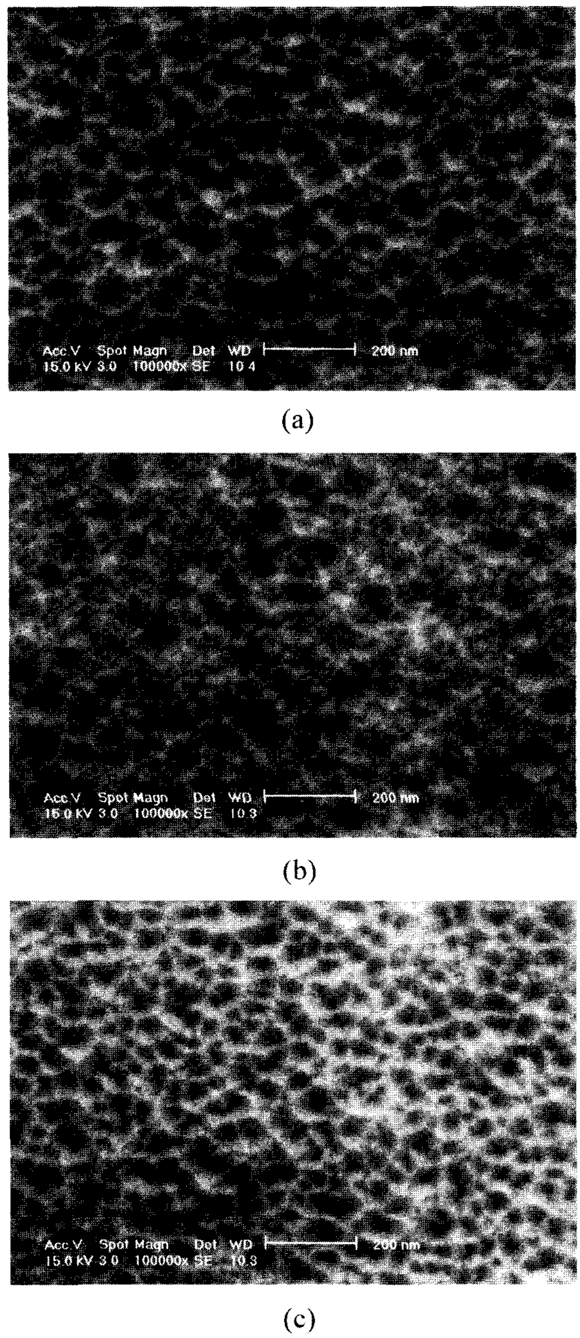
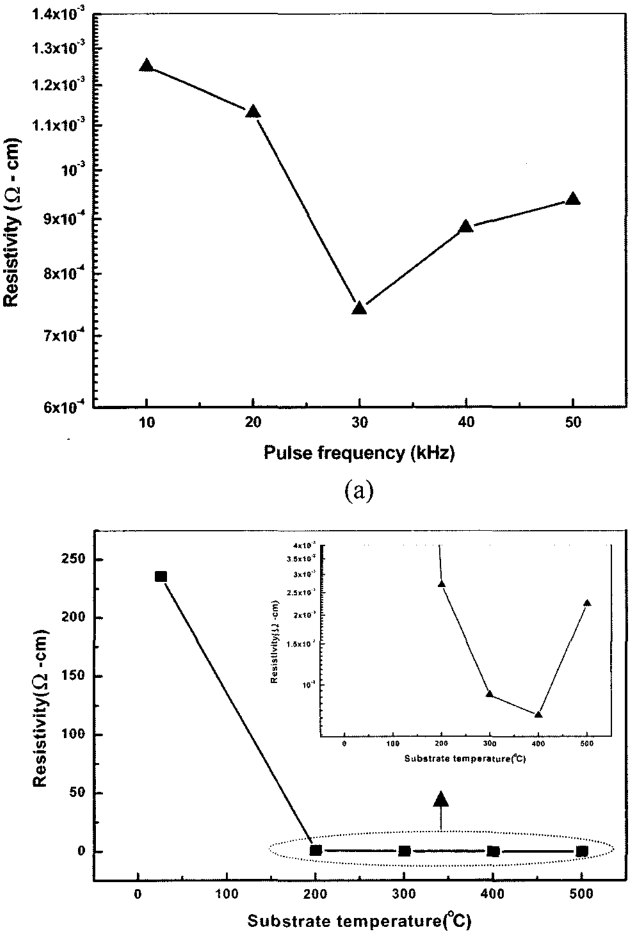


Fig. 3. SEM micrograph of AZO films prepared as a function of pulse frequency: (a) 10 kHz, 400°C, (b) 30 kHz, 400°C, and (c) 50 kHz, 400°C.



(b)

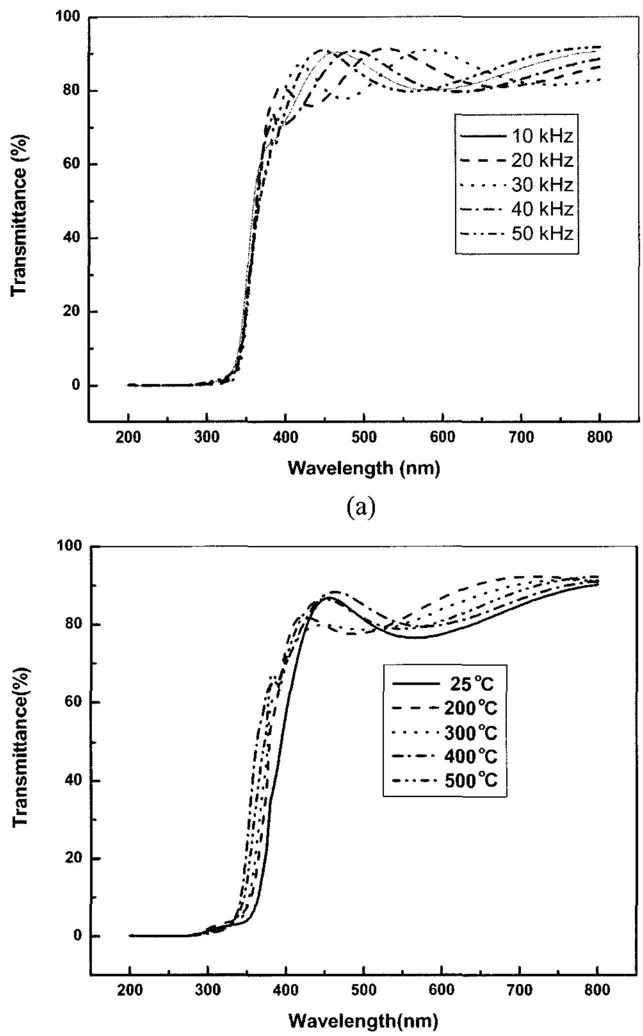
Fig. 4. The electrical resistivity of AZO films prepared at different pulse frequency (a) on the substrate temperature of 400°C under 5 mTorr, and at different substrate temperature (b) on the pulse frequency of 30 kHz under of 5 mTorr.

is, the increase of pulse frequency allows the sputtered atoms to move into more stable sites of substrate surface, which makes the grains bigger in size and defects less in number [5]. This is why the resistivity of AZO films decrease with the increase of pulse frequency. However, when higher pulse frequency than 30 kHz was applied, it could be assumed that the resistivity increased slightly due to the increased kinetic energy of sputtered particles, leading to the increase of defect density on the film surface [21].

Figure 4b shows the resistivitiy of AZO films prepared at different substrate temperature. The resistivity of the films decreased with increasing substrate temperatures from 25 to 400°C and the minimal value was 7.40×10^{-4} Ω-cm at the substrate temperature of 400°C. A further increase in the substrate temperature resulted in the increase of resistivity. The decrease of the resistivity at the substrate temperature of 400°C is attributed to a decrease in absorption of oxygen resulting in the decrease of the electron traps, while the increase of resistivity at 500°C is attributed to decrease of oxygen defect resulting in the decrease of carrier concentration [5].

3.3. Optical properties

The optical transmittance of AZO films deposited at different pulse frequencies was investigated in the wavelength from 200 to 800 nm, as shown in Fig. 5a. The optical transmittance in the range of visible light was about 85~90 % regardless of pulse frequency, which indicated very transparent AZO thin films. All the films also exhibited interference fringes of the spectra with



(b)

Fig. 5. The optical transmittance spectra of AZO films prepared at different pulse frequency (a) on the substrate temperature of 400°C under 5 mTorr, and at different substrate temperature (b) on the pulse frequency of 30 kHz under 5 mTorr.

deep valleys, which indicated a smooth surface in the film [6]. Figure 5b shows the optical transmittance of AZO films prepared as a function of substrate temperature. All the films exhibited a visible transmittance of 80~90 % at the wavelength from 400 to 800 nm, even though the film prepared at 25°C has relatively low transparency. The low optical transmittance of films prepared at 25°C is due to low adatom mobility at low substrate temperature [5]. The optical absorption edge moved to the left as the substrate temperature increased from 25 to 400°C. However, it moved to the right again as the substrate temperature increased from 400 to 500°C.

4. Conclusions

AZO thin films with low resistivity and high optical transmittance could be prepared on glass by pulsed DC magnetron sputtering. XRD analysis indicated that AZO films were highly oriented along c-axis perpendicular to substrate surface, and almost independent on the pulse frequency. It also showed that the crystallinity of the films were strongly dependent on substrate temperature. The AZO film prepared at the substrate temperature of 400°C and pulse frequency of 30 kHz showed the lowest resistivity of 7.40×10^{-4} Ω-cm as well as the smoothest and densest surface morphology. It was found that the decreased of film resistivity resulted from the improvement of c-axis crystallinity, leading to the decrease of surface roughness. The optical transmittance spectra of the films showed a very high transmittance of 85~90 % in the visible wavelength region. The characteristics of the low electrical resistivity and high optical transmittance of AZO films suggested a possible application for transparent conducting oxides.

Acknowledgement

This works supported by the ministry of science and technology, Korea Science and Engineering Foundation (KOSEF) through Advanced Material Process of Information Technology (AMPIT) at Sungkyunkwan University (grant No. R12-2002-057-01001-0).

Reference

[1] X. Jiang, F.L. Wong, M.K. Fung and S.T. Lee, "Aluminum-doped zinc ode films as transparent conductive electrode for organic light-emitting devices", Appl. Phys. Lett. 83(9) (2003) 1875.

[2] Z.L. Pei, C. Sun, M.H. Tan, J.Q. Xiao, D.H. Guan, R.F. Huang and L.S. Wen, "Optical and electrical properties of direct-current magnetron sputtered ZnO : Al films", Appl. Phys. Lett. 90(7) (2001) 3432.

[3] Z.C. Jin, I. Hamberg and C.G. Granqvist, "Optical properties of transparent and heat reflecting ZnO : Al films made by reactive sputtering", Appl. Phys. Lett. 51(3) (1987) 149.

[4] R. Cebulla, R. Wendt and K. Ellmer, "Al-doped zinc oxide films deposited by simultaneous rf and dc excitation of a magnetron plasma: Relationships between plasma parameters and structural and electrical film properties", J. Appl. Phys. 83(2) (1998) 1087.

[5] E.-G. Fu, D.-M. Zhuang, G. Zhang, Z. Ming, W.-F. Yang and J.-F. Liu, "Properties of transparent conductive ZnO : Al thin films prepared by magnetron sputtering", Microelectronics Journal 35 (2004) 383.

[6] D. Song, A. G. Aberle and J. Xia, "Optimisation of ZnO : Al films by change of sputter gas pressure for solar cell application", Appl. Surf. Sci. 195(4) (2002) 291.

[7] J.-M. Ting and B.S. Tsai, "DC reactive sputter deposition of ZnO : Al thin film on glass", Mater. Chem. Phy. 72(2) (2001) 273.

[8] F. Quaranta, A. Valentini and F.R. Rizzi, "Dual-ion-beam Sputter Deposition of ZnO Films", J. Appl. Phys., J. Appl. Phys. 74(1) (1993) 247.

[9] A.J.C. Fiddes, K. Durose and A.W. Brinkman, "Preparation of ZnO films by spray pyrolysis", J. Cryst. Growth 159(1) (1996) 210.

[10] M. Ohyama, H. Kozuka and T. Yoko, "Sol-gel preparation of ZnO films with extremely preferred orientation along (002) plane from zinc acetate solution", Thin Solid Films 306(1) (1997) 78.

[11] V. Cracium, J. Elders and J.G.E. Gardeniers, "Characteristics of high quality ZnO thin films deposited by pulsed laser deposition", Appl. Phys. Lett. 65(23) (1994) 2963.

[12] S.K. Ghandhi, R.J. Field and J.R. Shealy, "Highly oriented zinc oxide films grown by the oxidation of diethylzinc", Appl. Phys. Lett. 37(5) (1980) 449.

[13] S.-S. Lin, J.-L. Huang and D.-F. Lii, "The effects of r.f. power and substrate temperature on the properties of ZnO films", Sur. Coat. Tech. 176(2) (2004) 173.

[14] F.K. Shan and Y.S. Yu, "Band gap energy of pure and Al-doped ZnO thin films", J. Eur. Ceram. Soc. 24(6) (2004) 1869.

[15] D.H. Zhang, Q.P. Wang and Z.Y. Xue, "Photoluminescence of ZnO films excited with light of different wavelength", Appl. Surf. Sci. 207 (2003) 20.

[16] Q.P. Wang, D.H. Zhang, H.L. Ma, X.H. Zhang and X.J. Zhang, "Photoluminescence of ZnO films prepared by r. f. sputtering on different substrates", Appl. Surf. Sci. 220 (2003) 12.

[17] F. Chaabouni, M. Abaab and B. Rezig, "Effect of the substrate temperature on the properties of ZnO films grown by RF magnetron sputtering", Mater. Sci. Eng. B 109 (2004) 236.

[18] P.J. Kelly, C.F. Beevers, P.S. Henderson, R.D. Arnell,

J.W. Bradley and H. Backer, "A comparison of the properties of titanium-based films produced by pulsed and continuous DC magnetron sputtering", Sur. Coat. Tech. 174-175 (2003) 795.

[19] F. Fenske, P. Reinig, B. Selle and W. Fuhs, "Pulse-sputter deposition of highly <100>-oriented crystalline silicon films", Sur. Coat. Tech. 174-175 (2003) 801.

[20] K. Koski, J. Holsa and P. Juliet, "Surface defects and generation in reactive magnetron sputtering of aluminium oxide thin films", Sur. Coat. Tech. 115 (1999) 163.

[21] E.V. Barnat and T.-M. Lu, "Pulsed and pulsed bias sputtering principles and applications", Kluwer Academic Publishers, USA (2003) p.109.