



# Annealing effects of co-doping with Al and Sb on structure and optical–electrical properties of the ZnO thin films

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## ABSTRACT

The ZnO thin films co-doped with Al and Sb have been successfully deposited by a sol–gel spin-coating method on glass substrates and annealed at different temperature for 2 h in air. The annealing effects of different temperature on the structure and biaxial stress were characterized by X-ray diffraction. The results revealed that the annealed ZnO thin films mainly consist of ZnO with wurtzite structure, and the biaxial stress is lower during annealing at 550 °C. The annealed films have high transmittance in the visible region and show sharp absorption edges in the UV region. The optical band gap  $E_g$  values are 2.95, 3.03, 3.18 and 3.15 eV, which corresponding to the films annealed at 450, 500, 550, 600 °C, respectively. The resistivity of thin films reaches a minimum when the annealing temperature at 550 °C. The conducting mechanism is contributed to Sb substitute for Zn inducing two corresponding Zn vacancies.

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## 1. Introduction

ZnO possesses a wide direct band gap energy of 3.37 eV and a large exciton binding energy of 60 meV [1–3], which is a very attractive material for optoelectronic applications [4]. ZnO thin films have been prepared by various methods such as RF magnetron sputtering [5], molecular beam epitaxy (MBE) [6], metal organic chemical vapor deposition (MOCVD) [7], pulsed laser deposition (PLD) [8], spray pyrolysis [9] and the sol–gel process [10]. The ZnO thin films doped with some elements and prepared by sol–gel technique have now been especially paid attention owing to its advantages such as low cost, simple deposition procedure, easier composition control, low processing temperature, easier fabrication of large area films.

To realize such optoelectronic devices, it is required to control the carrier density and band gap of thin films, which can be adjusted by co-doping of donor and acceptor. The deliberate co-doping of donors with acceptor is essential for the enhancement of the solubility of the acceptors with the stabilization of the ionic charge distributions and the reduction of acceptor binding energy [11].

On the basis of this idea, several co-doping techniques have been reported to prepare p-type ZnO films, such as the co-doping of P and Ga by magnetron sputtering, N and In by ion beam enhanced deposition method, N and Al by RF magnetron sputtering, etc. [12–14]. Among the various candidate materials for realizing high conductivity p-type of ZnO, Sb incorporated ZnO is of current interest because Sb would substitute for Zn instead of oxygen and then produce two corresponding Zn vacancies suggested by Limpijum-nong et al. [15]. Ilcan et al. [16] reported on ZnO thin films doped with Sb grown by a sol–gel method. Annealing treatment greatly affects the film properties, such as crystal quality, optical and electric property. So far, however, there is little detail report on the annealing effects of different temperature on the properties of the ZnO films co-doped with Al and Sb, and deposited by a sol–gel spin-coating method. In this paper, we have reported the annealing effects of different temperature on the structure, biaxial stress, surface morphology, optical and electrical properties of the ZnO thin films co-doped with Al and Sb.

## 2. Experimental details

The ZnO thin films co-doped with Al and Sb were deposited onto glass substrates by the sol–gel spin-coating method. Zinc acetate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] was used as a starting material. Ethylene glycol monomethyl ether ( $\text{C}_3\text{H}_8\text{O}_2$ ), ethanolamine ( $\text{C}_2\text{H}_7\text{NO}$ ), aluminium chloride ( $\text{AlCl}_3$ ) and antimony trichloride ( $\text{SbCl}_3$ ) were used as solvent, stabilizer, dopant source, respectively. According to the co-doping result

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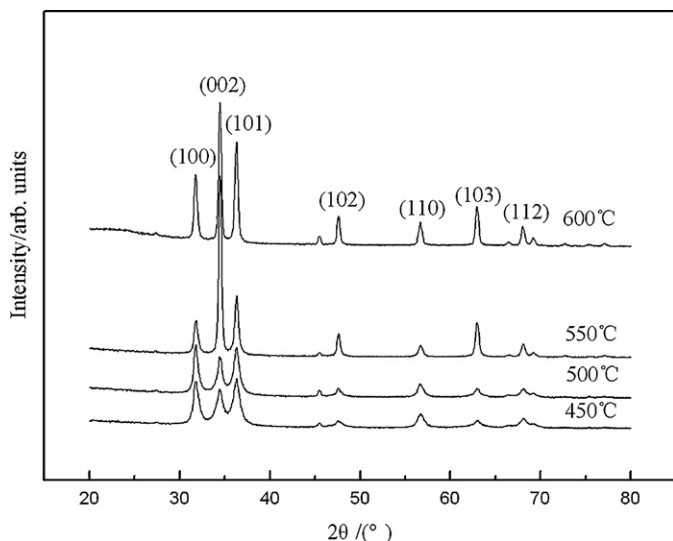


Fig. 1. XRD patterns of ZnO films at different annealing temperatures.

[11], the molar ratio of ethanolamine to zinc acetate and  $\text{AlCl}_3$  to  $\text{SbCl}_3$  were maintained at 1:1 and 1:2, respectively. The concentration of the solutions is 0.8 mol/L. Requisite amounts of  $\text{SbCl}_3$  added to zinc acetate to obtain sols with 1.0% Sb–Zn molar ratio. The obtained mixture was stirred at 60 °C for 4 h to yield a clear and homogeneous solution, which was then served as the coating source after cooling down to room temperature. The glass substrates were first cleaned by a detergent, and then in methanol and acetone each for 30 min by using an ultrasonic cleaner. Finally, the glass substrates were rinsed with deionized water and dried in oven. The coating solution was dropped onto a glass substrate, which was rotated at 3000 rpm for 30 s using KW-4A spin coater. After the spin-coating, the film was dried at 300 °C for 20 min in a furnace to evaporate the solvent and to remove organic residuals. This coating/drying process was repeated for five times before the film was inserted into a furnace and annealed in air. This coating process was applied for all samples.

The crystal graphic interpretations were performed by Rigaku D/MAX-RB X-ray diffractometer (XRD) using  $\text{Cu K}\alpha$  wavelength ( $\lambda = 0.15406 \text{ nm}$ ) and scanning in  $2\theta$  range from 20° to 80°. Surface morphology and thickness of the film were studied using an FEI-SIRION scanning electron microscope (SEM). Optical transmittance was recorded with a double beam TU-1901 UV–vis spectrophotometer in the wavelength range 280–850 nm. The conductivity measurements were performed with four probe method.

### 3. Results and discussion

#### 3.1. Crystal structure

Fig. 1 shows the XRD patterns of the Al and Sb co-doped ZnO thin films with the concentration of 1.5 at.% annealed at different temperatures for 2 h in air (here, the molar ratio of Al to Sb was always maintained at 1:2) prepared by sol–gel technique. As indexed in the figure, diffraction peaks are basically attributed to the wurtzite structure of ZnO (JCPDS 76-0704). The diffraction peaks of 46° could be peak (2 0 2) of  $\text{Al}_2\text{O}_3$ . Moreover, the ZnO films annealed at different temperatures have different diffraction peaks of ZnO, and the (002) peaks enhance significantly compared with the other two peaks (1 0 0) and (1 0 1) with the increasing temperature. Also, the intensity of all diffraction peaks enhances at higher annealing temperature, because higher temperature provides more energy to enhance the atom mobility resulting in an improvement in the quality and crystallinity of the films within a certain temperature.

From Fig. 1, average crystallite size is approximately calculated by Scherrer formula.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $D$  is crystallite size,  $K$  is constant of 0.89,  $\lambda$  is X-ray wavelength (0.15406 nm),  $\beta$  is full width at half maximum,  $\theta$  is diffraction angle, respectively. The (002) peaks were used to calculate the average crystallite size. The calculated average crystallite sizes of the Al and Sb co-doped ZnO thin films with the concentration of

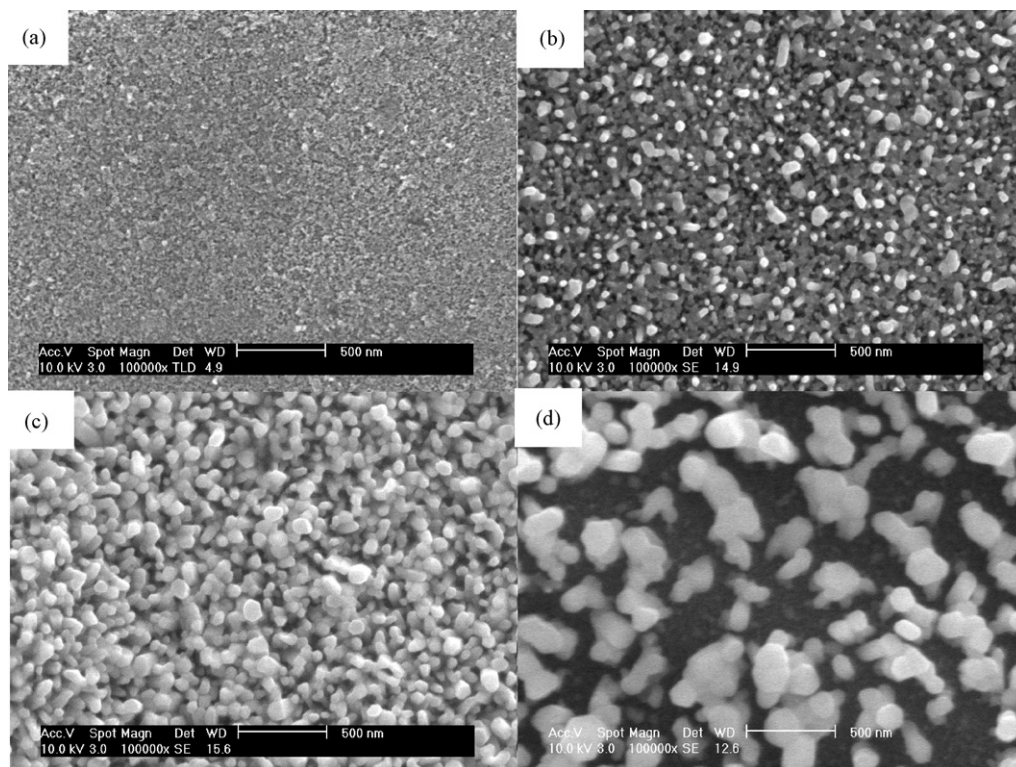


Fig. 2. SEM micrographs of the ZnO films co-doped with Al and Sb in the concentration of 1.5 at.% and annealed at different temperatures (a) 450 °C, (b) 500 °C, (c) 550 °C, (d) 600 °C.

1.5 at.% are of 10.97, 12.71, 13.32, 15.42 nm, which correspond to the films annealed at 450, 500, 550, 600 °C, respectively.

According to the hexagonal symmetry, the lattice constant can be calculated by the following formula.

$$d = \frac{1}{\sqrt{\frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2}}} \quad (2)$$

where  $d$  is interplanar distance,  $h, k, l$  are crystal plane index,  $a, b, c$  are cell parameter, respectively.

The biaxial stress along the  $c$ -axis was calculated by using the following formula [17].

$$\sigma = -453.6 \times 10^9 \left[ \frac{(c - c_0)}{c_0} \right] \quad (3)$$

where  $c$  is the lattice parameter of the strained ZnO films calculated from X-ray diffraction data and  $c_0$  is the strain-free lattice parameter ( $c_0 = 0.5206$  nm) (JCPDS, 36-1451). From formula of (2) and (3), the calculated biaxial stress of the Al and Sb co-doped ZnO thin films with the concentration of 1.5 at.% are of  $3.49 \times 10^8$ ,  $2.30 \times 10^8$ ,  $1.03 \times 10^8$ ,  $6.38 \times 10^8$  Pa, which corresponding to the annealing temperature at 450, 500, 550, 600 °C, respectively. The biaxial stress reduces with the increase of the annealing temperature and reaches a minimum at 550 °C, and then enhances with further increasing of temperature, which indicates that annealing treatment can reduce the biaxial stress of thin films. The biaxial stress is significantly larger for the sample that was annealed at 600 °C could be uneven structure distribution caused by higher annealing temperature. The magnitude of calculated biaxial stress is accordance with that of Ref. [17], and biaxial stress is smaller during annealing at 550 °C.

### 3.2. Surface morphology

Fig. 2 shows SEM photographs of the Al and Sb co-doped ZnO thin films with the concentration of 1.5 at.% prepared by sol-gel technique annealing at different temperatures for 2 h in air. It is found that the surface appears flatter, and crystal grain distributes uniformly and appears small. The crystallite size of thin films become larger with the increasing of annealing temperature and the crystallite size for the as-deposited samples is about 20–50 nm. At high temperature, the atoms have sufficient diffuse activation energy to occupy the correct site in the crystal lattice and grains with the lower surface energy will become larger [18]. Then the growth orientation develops into one crystallographic direction of the low surface energy, leading to the increases of ZnO grain sizes. For comparison, the grain size of the ZnO films analyzed by SEM is much larger than that of the data obtained by XRD. This difference might be because the grain size measured from SEM is the surface morphology instead of the single crystal, and the grain size measured from XRD is single crystal along thickness direction of thin films.

### 3.3. Optical properties

Fig. 3 shows the transmittance spectra of the Al and Sb co-doped ZnO thin films with the concentration of 1.5 at.% annealed at different temperatures for 2 h in air. For all the films, they have high transmittance in the visible region and show sharp absorption edges in the UV region. The ZnO thin films co-doped with Al and Sb have the highest transmittance at 550 °C and the lowest transmittance at 450 °C in the visible region, indicating gaining higher crystallinity and optical quality. Higher transmittance in visible region indicates that the film has less defects and better crystallinity [19].

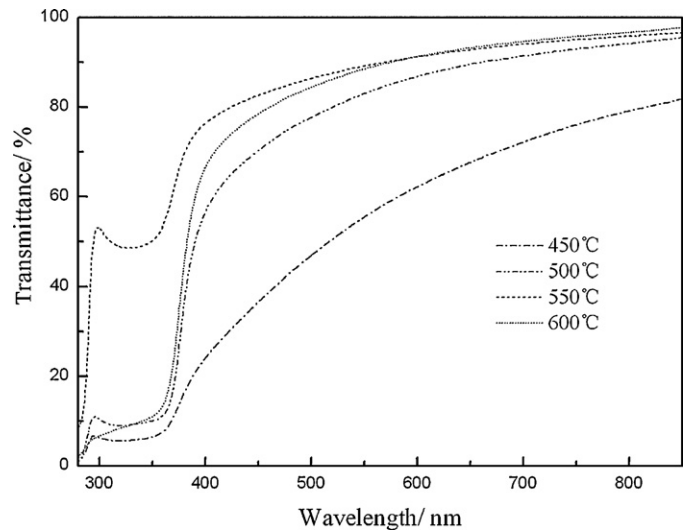


Fig. 3. Optical transmittance spectra of ZnO thin films.

Optical band gap of the ZnO thin films can be obtained by applying the following two formulae (4) and (5) [20,21].

$$T = (1 - R)^2 \exp(-\alpha d) \quad (4)$$

$$\alpha h\nu = D(h\nu - E_g)^{1/2} \quad (5)$$

In the formula (4),  $T$  is the transmittance of the ZnO thin film,  $R$  is its reflectivity,  $\alpha$  is the absorption coefficient and  $d$  is the film thickness. In the formula (5),  $h\nu$  is the photon energy,  $D$  is a constant and  $E_g$  is the optical band gap. According to formulae of (4) and (5), the absorption coefficient was calculated by using  $\alpha \sim \ln T$  as well as  $\alpha h\nu \sim (h\nu - E_g)^{1/2}$ . Then the plot of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) can be obtained. Extrapolation of linear portion to the energy axis at  $(\alpha h\nu)^2 = 0$  gives the  $E_g$  value (Fig. 4).

By the above process, the  $E_g$  values are 2.95, 3.03, 3.18 and 3.15 eV, which corresponding to the annealing temperature at 450, 500, 550, 600 °C, respectively. We believe that the changes of  $E_g$  originate from varied carrier concentration due to the co-doping of Al and Sb.

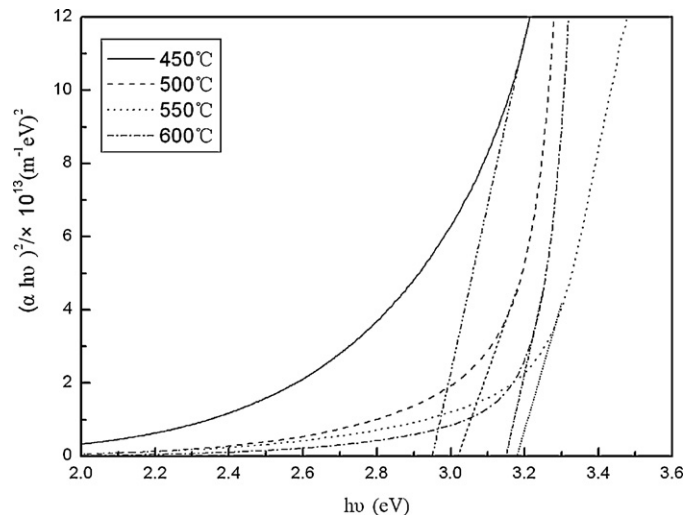


Fig. 4. Plot of  $(\alpha h\nu)^2$  vs.  $h\nu$  of the ZnO thin films annealed at different temperatures.

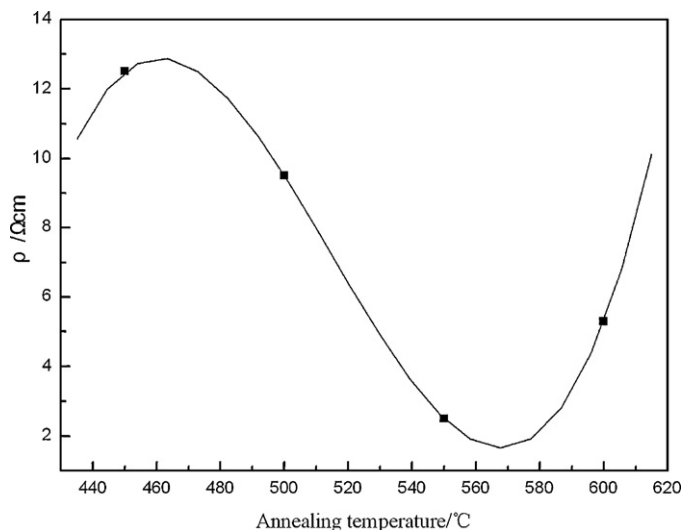


Fig. 5. Electrical resistivity of ZnO thin films co-doped with Al and Sb.

### 3.4. Electrical properties

The electrical characteristics of the ZnO thin films can be controlled by doping with ternary elements or by adjusting process conditions. The resistivity of the films is calculated using the following equation [22]:

$$\rho = \frac{\pi t}{\ln 2} \frac{V}{I} \quad (6)$$

where  $t$  is the thickness of the sample,  $V$  is the voltage and  $I$  is the current.

Fig. 5 shows the electrical resistivity of the Al and Sb co-doped ZnO thin films with the concentration of 1.5 at.% annealed at different temperature for 2 h in air. The results indicate that the resistivity of ZnO thin films co-doped with Al and Sb reduces with the increase of annealing temperature and reaches a minimum, 2.5 Ω cm, at 550 °C, and then enhances with further increasing of temperature.

To explain the electrical behavior of thin films described above, there are some reasons, such as Al and Sb-co-doping, crystallite size and growth orientation. Limpijumnong et al. [15] suggested that Sb would substitute for Zn instead of oxygen and then produce two corresponding Zn vacancies, and pointed out that the  $\text{Sb}_{\text{Zn}}-2\text{V}_{\text{Zn}}$  complex was believed to be the most likely candidate to form a shallow acceptor level in large size mismatched group-V-doped ZnO. Furthermore, the grain boundaries have a large effect on the electrical properties. Indeed, when the crystallite size increases, the density of grain boundaries decreases and the mobility of thin films reduces. In contrast, when the crystallite size decreases, the scattering by grain boundary becomes preponderant and causes a decrease in the mobility. Therefore, we have got a preferable mobility at an appropriate annealing temperature of 550 °C.

## 4. Conclusions

The Al and Sb co-doped ZnO thin films with concentration of 1.5 at.% have been deposited by a sol-gel spin-coating method. All thin films were annealed for 2 h in air in the temperature range from 450 to 600 °C. The effects of annealing temperature on the structure, biaxial stress, surface morphology, optical and electrical properties of the ZnO thin films co-doped with Al and Sb were investigated. XRD analysis revealed that the annealed ZnO thin films mainly consist of ZnO with wurtzite structure and show the  $c$ -axis grain orientation. Annealing treatment can reduce the biaxial stress of thin films. SEM analysis indicated that surface of thin films appears flatter, and crystal grain distribute uniformly and appears small. The annealed films have high transmittance in the visible region and show sharp absorption edges in the UV region. The absorption coefficient analysis showed that the optical band gap energy,  $E_g$ , for the ZnO thin films were between 2.95 and 3.18 eV. The resistivity of thin films reaches a minimum when the annealing temperature at 550 °C. These results suggest that the Al and Sb co-doped ZnO thin films prepared by sol-gel spin-coating process have good crystal structure, optical and electrical properties.

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## References

- [1] K.J. Chen, F.Y. Hung, S.J. Chang, S.J. Young, *J. Alloys Compd.* 479 (2009) 674.
- [2] Y.W. De, J. Zhou, G.Z. Liu, *J. Alloys Compd.* 481 (2009) 802.
- [3] N. Gopalakrishnan, B.C. Shin, K.P. Bhuvana, J. Elanchezhian, T. Balasubramanian, *J. Alloys Compd.* 465 (2008) 502.
- [4] S.W. Xue, X.T. Zu, W.L. Zhou, H.X. Deng, X. Xiang, L. Zhang, H. Deng, *J. Alloys Compd.* 448 (2008) 21.
- [5] C.S. Hsi, B. Houg, B.Y. Hou, G.J. Chen, S.L. Fu, *J. Alloys Compd.* 464 (2008) 89.
- [6] Z.L. Lu, W. Miao, W.Q. Zou, M.X. Xu, *J. Alloys Compd.* 494 (2010) 392.
- [7] H. Lin, S.M. Zhou, T.H. Huang, H. Teng, X.D. Liu, S.L. Gu, S.M. Zhu, Z.L. Xie, P. Han, R. Zhang, *J. Alloys Compd.* 467 (2009) L8.
- [8] J.H. Kim, D.H. Cho, W.Y. Lee, B.M. Moon, W. Bahng, S.C. Kim, N.K. Kim, S.M. Koo, *J. Alloys Compd.* 489 (2010) 179.
- [9] C.E. Benouis, M. Benhaliliba, A. Sanchez Juarez, M.S. Aida, F. Chami, F. Yakuphanoglu, *J. Alloys Compd.* 490 (2010) 62.
- [10] S.K. Neogi, R. Ghosh, G.K. Paul, S.K. Bera, S. Bandyopadhyay, *J. Alloys Compd.* 487 (2009) 269.
- [11] T. Yamamoto, *Thin Solid Films* 420 (2002) 100.
- [12] Q.P. Wang, Z. Sun, J. Du, P. Zhao, X.H. Wu, X.J. Zhang, *Opt. Mater.* 29 (2007) 1358.
- [13] N.Y. Yuan, L.N. Fan, J.H. Li, X.Q. Wang, *Appl. Surf. Sci.* 253 (2007) 4990.
- [14] K.P. Bhuvana, J. Elanchezhian, N. Gopalakrishnan, B.C. Shin, T. Balasubramanian, *J. Alloys Compd.* 478 (2009) 54.
- [15] S. Limpijumnong, S.B. Zhang, S.H. Wei, C.H. Park, *Phys. Rev. Lett.* 92 (2004) 155504.
- [16] S. Ilican, Y. Caglar, M. Caglar, F. Yakuphanoglu, J.B. Cui, *Physica E* 41 (2008) 96.
- [17] W.T. Lim, C.H. Lee, *Thin Solid Films* 353 (1999) 12.
- [18] S.Y. Hu, Y.C. Lee, J.W. Lee, J.C. Huang, J.L. Shen, W. Water, *Appl. Surf. Sci.* 254 (2008) 1578.
- [19] M. Rusop, K. Uma, T. Soga, T. Jimbo, *Mater. Sci. Eng. B* 127 (2006) 150.
- [20] L.H. Xu, X.Y. Li, J. Yuan, *Superlattices Microstruct.* 44 (2008) 276.
- [21] L.P. Peng, L. Fang, X.F. Yang, Y.J. Li, *J. Alloys Compd.* 484 (2009) 575.
- [22] H.P. Yang, *A Study of P-type Zinc Oxide Thin Films*, McGill University, Montreal, Canada, 2006, pp. 40.