

Influence of oxygen/argon ratio on structural, electrical and optical properties of Ag-doped ZnO thin films

R. Deng^{a,b}, B. Yao^{a,b,*}, Y.F. Li^b, T. Yang^a, B.H. Li^b, Z.Z. Zhang^b, C.X. Shan^b, J.Y. Zhang^b, D.Z. Shen^b

^a Key State Lab of Superhard Material, and Department of Physics, Jilin University, Changchun 130023, People's Republic of China

^b Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

ARTICLE INFO

Article history:

Received 19 December 2009

Received in revised form

22 February 2010

Accepted 26 February 2010

Communicated by M. Kawasaki

Available online 10 March 2010

Keywords:

A1. X-ray diffraction

A3. Magnetron sputtering

B1. Oxides

B2. Semiconducting II–VI materials

ABSTRACT

Ag-doped ZnO (ZnO:Ag) thin films were deposited on quartz substrates by radio frequency magnetron sputtering technique. The influence of oxygen/argon ratio on structural, electrical and optical properties of ZnO:Ag films has been investigated. ZnO:Ag films gradually transform from n-type into p-type conductivity with increasing oxygen/argon ratio. X-ray photoelectron spectroscopy measurement indicates that Ag substitutes Zn site (Ag_{Zn}) in the ZnO:Ag films, acting as acceptor, and being responsible for the formation of p-type conductivity. The presence of p-type ZnO:Ag under O-rich condition is attributed to the depression of the donor defects and low formation energy of Ag_{Zn} acceptor. The I – V curve of the p-ZnO:Ag/n-ZnO homojunction shows a rectification characteristic with a turn-on voltage of ~ 7 V.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

ZnO is a promising semiconductor material in the field of ultraviolet (UV) light-emitting diodes (LEDs), laser diodes (LDs) and detectors because of its direct wide band gap and high exciton binding energy (60 meV) at room temperature (RT) [1–3]. Although ZnO has several advantages compared to GaN, the difficulty of p-type doping inhibits applications to optoelectronic devices. There have been many attempts to obtain the p-type ZnO by using various dopants, for example, group I and V elements of Li, Na, N, P and Sb [4–8]. Up to now, although electroluminescence (EL) of LED based on p-ZnO thin film has been realized, p-type ZnO has still some serious problems, such as irreproducibility and instability. One of the most important facts resulting in these problems is that a large number of native donor defects, such as interstitial zinc (Zn_i) and vacancy oxygen (V_O), strongly compensate the acceptor dopants, especially under O-poor condition [9]. Recent experimental and theoretical studies indicate that, an O-rich growth ambient is required for depressing formation of native donor defects [10]. However, under O-rich condition, the formation energies of some acceptor dopants substitutional O sites, such as N substitutional O site (N_O), are higher than that at Zn-rich condition due to high chemical activity of oxygen [11].

Hence, some researchers have been looking for appropriate doping methods to decrease formation energy of acceptor and depress native donor defects. Yan et al. [12] have predicted that the Ag_{Zn} defects in ZnO have much lower formation energy under O-rich condition by first-principle method, indicating O-rich condition benefits for p-type doping in ZnO. However, to our knowledge, there is few studies on the effect of oxygen/argon ratio on properties of ZnO:Ag thin films.

In the present work, ZnO:Ag thin films were grown on quartz substrates by ratio frequency (rf) magnetron sputtering. The influence of oxygen/argon ratio on structural, electrical and optical properties of the ZnO:Ag thin films were investigated.

2. Experiment

The ZnO:Ag thin films were grown on quartz substrates by ratio frequency (rf) magnetron sputtering. The target of ZnO containing Ag 2 at% was fabricated by sintering mixture of ZnO and Ag_2O powder. The sputtering was performed in an argon and oxygen mixture. During the process of thin films deposition, the total pressure was set to 1 Pa and the oxygen/argon ratio (here, P_{O_2} =oxygen flux/the total flux) was varied from 0 to 1.0. The substrate temperature was fixed at 250 °C. The sputtering power was 100 W, and the growth time was 60 min. All as-grown films show high resistivity, as listed in Table 1. For improving the electrical properties, all thin films were annealed at 650 °C under 10^{-3} Pa for 10 min.

* Corresponding author at: Key State Lab of Superhard Material, and Department of Physics, Jilin University, Changchun 130023, People's Republic of China. Tel.: +86 0431 6176355; fax: +86 0431 86171688.

E-mail address: yaobin196226@yahoo.com.cn (B. Yao).

Table 1
Room temperature electrical properties of annealed ZnO:Ag films grown at various P_{O_2} .

Samples	P_{O_2}	Carrier concentration n (cm^{-3})	Resistivity ρ ($\Omega \text{ cm}$)	Hall mobility μ (cm^2/Vs)	Carrier type
As-grown A–F	–	–	High resistivity	–	–
A	0	3.6×10^{18}	0.95	1.84	n
B	0.40	5.9×10^{17}	14.9	0.74	n
C	0.60	3.1×10^{17}	36.3	0.55	n
D	0.75	4.2×10^{17}	57.5	0.27	p
E	0.90	1.0×10^{18}	18.2	0.35	p
F	1.00	2.4×10^{16}	2.5×10^3	0.11	p

The structures of the thin films were characterized by X-ray diffraction (XRD) with Cu $K\alpha_1$ radiation ($\lambda=0.15406 \text{ nm}$). The chemical bonding states of the films were analyzed by XPS with Al anode as an X-ray source. The binding energy in the XPS spectra is calibrated by using that of C 1s (284.6 eV). Electrical properties were measured in the van der Pauw configuration by a Hall-effect measurement system. To obtain a reliable result, the magnetic field strength of 3, 6, 9, 12, 15 kG is adopted during the measurement processes. In the I – V character measurement, the metal Ni/Au and indium was used to fabricate the electrodes of ZnO:Ag and undoped ZnO, respectively. Photoluminescence (PL) measurement was performed using a He–Cd laser with 325 nm line as excitation source. All measurements were performed at RT.

3. Results and discussion

The electrical properties of all as-grown and annealed samples are shown in Table 1. Although all samples were annealed under the same condition, the electrical properties are different. This difference is due to the different growth conditions. It is found that the ZnO:Ag films grown at $0 \leq P_{O_2} < 0.75$ show n-type but p-type conductivity at $P_{O_2} \geq 0.75$. For the n-type ZnO films, with the increase of P_{O_2} , the resistivity increases from 0.95 to $36.3 \Omega \text{ cm}$ and electron concentration decreases from 3.6×10^{18} to $3.1 \times 10^{17} \text{ cm}^{-3}$. Generally, the electrical properties of ZnO are strongly dependent on the defect and impurity type. Zhang et al. [10] investigated the intrinsic defects in ZnO by first-principle method and found that the formation energies of donor defects, such as Zn_i and V_O , are higher in Zn-rich limit than that in O-rich limit. Meanwhile, Yan et al. [12] found that the formation energies of Ag substituting Zn site (Ag_{Zn}), as acceptor dopants, are very lower in O-rich limit than that in Zn-rich limit. Therefore, the decrease of electron concentration of the n-type ZnO films with increasing oxygen flux can be well understood as follows: with the increase of oxygen flux, (i) the donor defects are depressed and (ii) Ag_{Zn} concentration increases and compensates electrons. As P_{O_2} is above 0.75, the ZnO films transform from n-type into p-type conductivity. The hole concentration increases from 4.2×10^{17} to $1.0 \times 10^{18} \text{ cm}^{-3}$ when P_{O_2} increases from 0.75 to 0.9, in agreement with the Yan et al.'s [12] theoretical prediction. Recently, ionization energy of the Ag_{Zn} acceptor was determined to be 117 meV by temperature-dependent PL, which may be responsible for the high hole concentration [13]. However, the sample fabricated under pure oxygen condition ($P_{O_2}=1.0$) has a low hole concentration of $\sim 10^{16} \text{ cm}^{-3}$. This result seems to discrepancy with theoretical prediction that O-rich limit benefits for formation of p-type ZnO:Ag. Differing from ideal condition of theoretical calculation, in experiment, the grown ZnO under pure oxygen condition has very poor crystalline quality [14]. Such a grown condition results in the low quality ZnO film with a high resistivity $\sim 10^3 \Omega \text{ cm}$.

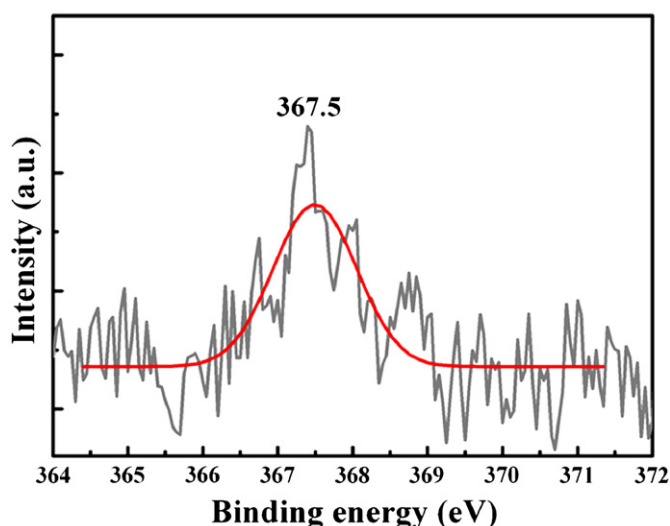


Fig. 1. XPS spectrum of the ZnO:Ag thin films grown at $P_{O_2}=0.75$.

To identify the chemical bonding states of Ag in the ZnO:Ag thin films, the XPS measurement was carried out. Fig. 1 shows XPS spectrum of the annealed ZnO:Ag film grown at $P_{O_2}=0.75$, where a peak is observed at 367.5 eV. It is reported that the binding energy of Ag $3d_{5/2}$ is in the range 368.1–368.4 eV for Ag^0 and 367.4–367.8 eV for Ag^+ ions [15,16]. Therefore, the 367.5 eV peak can be assigned to $\text{Ag}_{\text{Zn}}-\text{O}$ bonds, indicating that Ag occupies Zn site in the state of Ag^+ ion in the ZnO:Ag and acts as acceptor. This result provides a good confirmation of the conversion of carrier type. Furthermore, the Ag concentration in the ZnO:Ag is estimated to be 0.3% by a standard method in XPS measurement. The Ag concentration is lower than that in the target, which may be due to escape of Ag from sample as annealing at high temperature.

Fig. 2 illustrates the XRD patterns of undoped ZnO and the annealed ZnO:Ag films prepared on quartz substrates at various P_{O_2} . Only diffraction peaks of wurtzite ZnO are observed in the patterns, and no Ag_2O or Ag peaks are detected, indicating no obvious phase separation after annealing. All samples exhibit a (002) preferential orientation except the sample grown at $P_{O_2}=0$.

To get more information about the microstructure of the ZnO:Ag films, we calculate the lattice constant c with the data obtained from XRD. Fig. 3 plots the variation of the lattice constant c of the ZnO films as a function of P_{O_2} . For p-type samples at $P_{O_2} \geq 0.75$, the c -axis lattice constants are much larger than the value of 0.5203 nm of undoped ZnO. It has been reported that ZnO film grown on quartz is subjected to biaxial tensile stress due to large thermal mismatch between film and substrate, which result in decrease of the lattice constant c of the films [17]. Thus, the increase of the c -axis lattice constant cannot stem from stress but

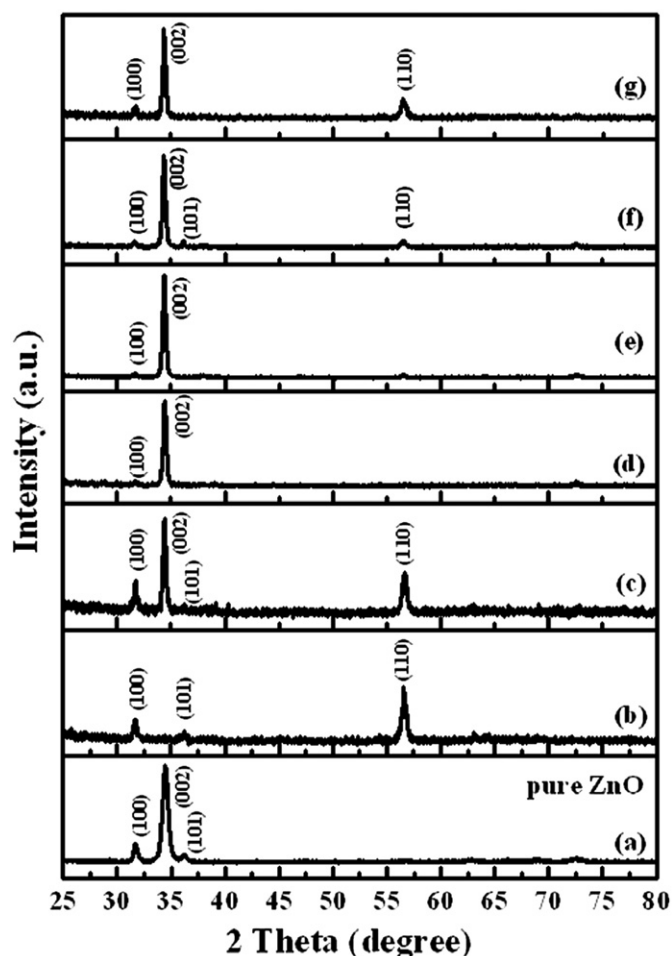


Fig. 2. XRD patterns of (a) undoped ZnO and annealed ZnO:Ag films prepared at various P_{O_2} : (b) 0; (c) 0.4; (d) 0.6; (e) 0.75; (f) 0.9 and (g) 1.0.

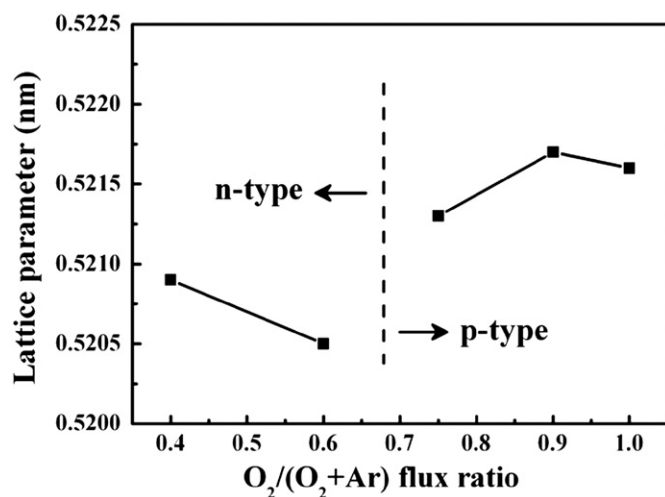


Fig. 3. The c-axis lattice constant of the ZnO:Ag films as a function of P_{O_2} .

substitution of some Ag for Zn in the films due to the larger ionic radius of Ag^+ (1.26 Å) than that of Zn^{2+} (0.74 Å) [18,19]. This result further confirms that Ag substitutes Zn sites in ZnO as acceptors. The results of both XPS and XRD reveal that the Ag has been doped into the ZnO thin films.

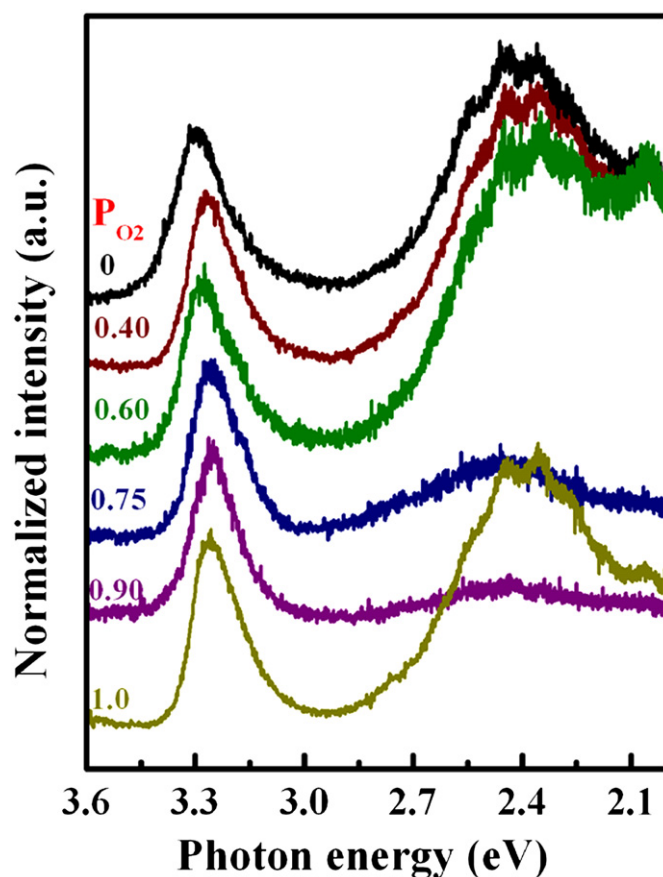


Fig. 4. RT PL spectra for the annealed ZnO:Ag films deposited at various P_{O_2} .

Fig. 4 shows RT PL spectra of the annealed ZnO:Ag films under different P_{O_2} . All spectra are composed of an emission peak in UV region and a broad emission band in visible region. The peaks at 3.25–3.3 eV are attributed to the near band edge emission (NBE). For the n-type ZnO film grown at $P_{O_2}=0$, the UV emission peak at 3.3 eV originates from the recombination emission of free-exciton. The PL peaks of the other n-type ZnO films located at 3.28–3.27 eV. However, for the p-type ZnO films, the UV PL peaks are located at 3.25 eV, obviously having a red-shift with respect to n-type ZnO films. The origin of the red-shift is not clear yet. We speculate that it may be from the emission of Ag-related defects. As reported by Wang et al. [19], the PL peak at 3.26 eV (380 nm) is due to donor-to-acceptor pairs (DAP). For the n-type ZnO films grown at low oxygen flux, the intensity of the green emission bands (GB) is stronger than that of the UV peaks. For the p-type ZnO films grown at $P_{O_2}=0.75$ and 0.9, the intensity of GB obviously weakens. However, for the p-type ZnO films grown at $P_{O_2}=1$, the intensity of GB becomes strong again. The broad GB is due to the emission of oxygen-related defects, such as oxygen vacancy (V_O , at 2.48 eV) and antisite oxygen (O_{Zn} , 2.40 eV) [20–22]. In the present work, the emission of the V_O and O_{Zn} is covered by the GB because it is very broad (full width of half maximum of 0.6 eV). Therefore, the origin of GB cannot be distinguished. However, taking the different P_{O_2} into consideration, the change of GB intensity can be well understood as follows: (i) the strong GB emission of the n-type ZnO films grown under low oxygen flux is assigned to V_O because of insufficient oxygen. (ii) For the p-type ZnO films grown at $P_{O_2}=1$, the strong GB originates from the O_{Zn} -related emission because of excess oxygen. (iii) The $P_{O_2}=0.75$ and 0.9 is suitable for depressing oxygen-related defects (V_O and O_{Zn}), resulting in weak GB emission.

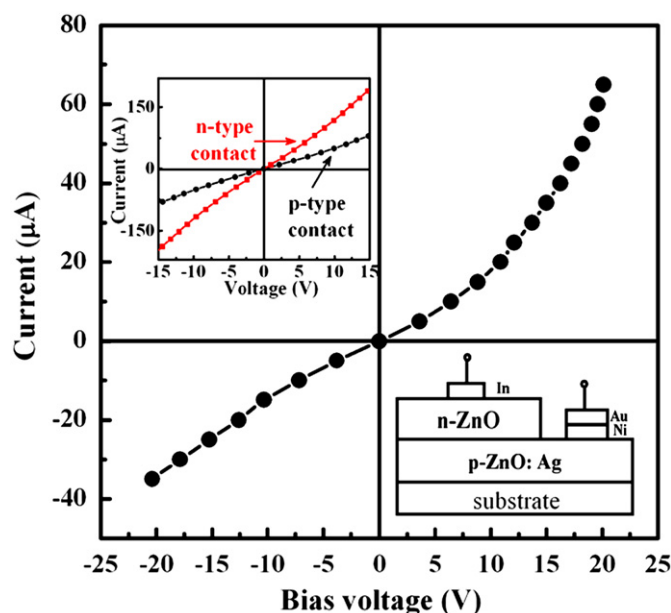


Fig. 5. I – V characteristics of the p-ZnO:Ag/n-ZnO homojunction. The bottom-right inset shows the schematic structure of the p–n junction. The upper-left inset shows the Ohmic contact of Ni/Au electrode on p-type layer and In on n-type layer.

Finally, to further examine the p-type conductivity, the n-type ZnO film was fabricated on the p-type ZnO film to form a p–n homojunction. The schematic structure of the ZnO p–n homojunction is shown in the bottom right inset in Fig. 5. The I – V curve of p-ZnO:Ag/n-ZnO homojunction was measured, as shown in Fig. 5. The I – V curve shows the characteristics of a nonlinear and rectifying diode with a turn-on voltage of ~ 7 V, which is larger than band gap of ZnO. The large turn-on voltage is due to large series resistance of homojunction, which was also reported in some literatures [23–25].

4. Summary

The conversion of the conductivity type has been realized in ZnO:Ag thin films by controlling oxygen/argon ratios, and p-type ZnO:Ag films with the low resistivity, high carrier concentration, and good photoluminescent properties were obtained by optimizing oxygen/argon ratio. The oxygen/argon ratio is important parameter for formation of p-type ZnO:Ag films. The O-rich

condition is favorite for the formation of p-type ZnO:Ag, but differing from theoretical prediction, pure oxygen sputtering is not a good growth condition to obtain p-type ZnO:Ag films with low resistivity. Furthermore, the p-ZnO:Ag/n-ZnO homojunction shows a good rectification characteristic in the I – V measurement.

Acknowledgments

This work was supported by the Key Project of National Natural Science Foundation of China under Grant no. 50532050, the “973” Program under Grant no. 2006CB604906, the Innovation Project of Chinese Academy of Sciences, and the National Natural Science Foundation of China under Grant nos. 60806002, 60506014, 10874178, 10674133, and 60776011.

References

- [1] T. Makino, C.H. Chia, T.T. Nguen, Y. Segawa, Appl. Phys. Lett. 77 (2000) 1632.
- [2] S.Y. Lee, E.S. Shim, H.S. Kang, S.S. Pang, J.S. Kang, Thin Solid Films 473 (2005) 31.
- [3] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science 292 (2001) 1897.
- [4] B. Yao, L.X. Guan, G.Z. Xing, Z.Z. Zhang, B.H. Li, Z.P. Wei, X.H. Wang, C.X. Cong, Y.P. Xie, Y.M. Lu, D.Z. Shen, J. Lumin. 122–123 (2007) 191.
- [5] Jae-Hong Lim, Chang-Ku Kang, Kyoung-Kook Kim, Il-Kyu Park, Dae-Kue Hwang, Seong-Ju Park, Adv. Mater. 18 (2006) 2720.
- [6] X.H. Wang, B. Yao, Z.Z. Zhang, B.H. Li, Z.P. Wei, D.Z. Shen, Y.M. Lu, X.W. Fan, Semicond. Sci. Technol. 21 (2006) 494.
- [7] J.M. Qin, B. Yao, Y. Yan, J.Y. Zhang, X.P. Jia, Z.Z. Zhang, B.H. Li, C.X. Shan, D.Z. Shen, Appl. Phys. Lett. 95 (2009) 022101.
- [8] S.S. Lin, J.G. Lu, Z.Z. Ye, H.P. He, X.Q. Gu, L.X. Chen, J.Y. Huang, B.H. Zhao, Solid State Commun. 148 (2008) 25.
- [9] D.C. Look, G.C. Farlow, Pakpoom Reunchan, Sukit Limpijumnon, S.B. Zhang, K. Nordlund, Phys. Rev. Lett. 95 (2005) 225502.
- [10] S.B. Zhang, S.H. Wei, A. Zunger, Phys. Rev. B 63 (2001) 075205.
- [11] E.-C. Lee, Y.-S. Kim, Y.-G. Jin, K.J. Chang, Phys. Rev. B 64 (2001) 085120.
- [12] Y.F. Yan, M.M. Al-Jassim, S.-H. Wei, Appl. Phys. Lett. 89 (2006) 181912.
- [13] M.A. Thomas, J.B. Cui, J. Appl. Phys. 105 (2009) 093533.
- [14] J.B. You, X.W. Zhang, Y.M. Fan, S. Qu, N.F. Chen, Appl. Phys. Lett. 91 (2007) 231907.
- [15] K.P. Liu, B.F.F. Yang, H.W. Yan, Z.P. Fu, M.W. Wen, Y.J. Chen, J. Zuo, Appl. Surf. Sci. 255 (2008) 2052.
- [16] PHI5300 Instrument Manual. USA: Perkin-Elmer Corporation, 1988.
- [17] Y.F. Li, B. Yao, Y.M. Lu, C.X. Cong, Z.Z. Zhang, Y.Q. Gai, C.J. Zheng, B.H. Li, Z.P. Wei, L. Xiao, S.C. Xu, Y. Liu, Appl. Phys. Lett. 91 (2007) 021915.
- [18] C.S. Hong, H.H. Park, J. Moon, H.H. Park, Thin Solid Films 515 (2006) 957.
- [19] X.B. Wang, C. Song, K.W. Geng, F. Zeng, F. Pan, J. Phys. D: Appl. Phys. 39 (2006) 4992.
- [20] P.M. Ratheesh Kumar, C. Sudha Kartha, K.P. Vijayakumar, F. Singh, D.K. Avasthi, T. Abe, Y. Kashiwaba, J. Appl. Phys. 97 (2005) 013509.
- [21] K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, J.A. Voigt, Appl. Phys. Lett. 68 (1996) 403.
- [22] T. Aoki, Y. Hatanaka, D.C. Look, Appl. Phys. Lett. 76 (2000) 3257.
- [23] G.T. Du, W.F. Liu, J.M. Bian, L.Z. Hu, H.W. Liang, X.S. Wang, A.M. Liu, T.P. Yang, Appl. Phys. Lett. 89 (2006) 052113.
- [24] Dae-Kue Hwang, Soon-Hyung Kang, Jae-Hong Lim, Eun-Jeong Yang, Jin-Yong Oh, Jin-Ho Yang, Seong-Ju Park, Appl. Phys. Lett. 86 (2005) 222101.
- [25] H.Y. Xu, Y.C. Liu, Y.X. Liu, C.S. Xu, C.L. Shao, R. Mu, Appl. Phys. B 80 (2005) 871.