Spray Pyrolysis Deposition of ZnO Thin Films from Zinc Chloride Precursor Solution at Different Substrate Temperatures

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Received: 21 September 2013 / Revised: 24 April 2014 / Published online: 18 November 2014
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Abstract ZnO films were prepared at different substrate temperatures through spraying pyrolysis deposition of zinc chloride precursor onto glass substrate. Substrate temperature affects surface morphology of films and therefore their optical and electrical properties. All films are polycrystalline with Wurtzite crystal structure and preferentially grow along c-axis direction. Formation of ZnO rods start at about 500 °C. The diameter and length of rods deposited at 500 °C are 350–500 and 550–700 nm, respectively. By increasing substrate temperature, film becomes more coverage and diameter of the rods reduces to 250–300 nm but their length increases to 1,000–1,200 nm, respectively. Optical transmission in visible region decreases with increasing substrate temperature. An ultraviolet emission and two visible emissions at 2.82 and 2.37 eV are observed for photoluminescence spectra at room temperature. The resistivity of ZnO films increases with increasing substrate temperature due to surface morphology.

KEY WORDS: ZnO; Rods; Spray pyrolysis; Substrate temperature; Surface morphology

1 Introduction

ZnO is one of the most important semiconductor materials with unique characteristic such as direct wide band gap of 3.37 eV, large exciton binding energy of 60 meV, low cost, nontoxic, chemical and mechanical stability, and high conductivity. These properties of ZnO make it be promising as a future material [1]. One-dimensional (1D) ZnO nanorods have attracted considerable attention since they provide much larger surface-to-volume ratio than bulk ZnO and ZnO films. In addition, ZnO nanorods due to their high

surface area, specific crystalline orientation, and directional transport to the conductive substrate are interested for using as a substrate in optoelectronic devices such as solar cells and detectors [2–4]. Because of these remarkable properties and applications, great efforts have been made to progress one-dimensional ZnO nanomaterials by different methods such as hydrothermal [5], vapor–liquid–solid (VLS) [6], chemical vapor transport and condensation (CVTC) [7], and physical vapor deposition (PVD) [8].

The properties of ZnO strongly depend on its morphologies and structures [9]. Thus, controlling the crystal morphologies of ZnO will greatly affect its applications in optoelectronic devices. Spray pyrolysis is a simple, low cost, vacuum less method and it is particularly attractive method for large scale films and microrods applications [10]. In the spray pyrolysis method, various parameters such as substrate temperature, precursor concentration, flow rate, and reaction time can affect the growth behavior [11]. In the previous works [12], it was found that ZnO rods can be grown by spray pyrolysis technique using aqueous solutions of zinc chloride at 500 °C, and the effect of precursor concentration

Available online at <http://link.springer.com/journal/40195>

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on optical, structural, and morphological properties of ZnO microrods was investigated. Krunk et al. [13] and Alver et al. [14] also synthesized ZnO rods by spray pyrolysis deposition technique, and it was reported that the temperature was the key factor for the formation of the ZnO rods.

In this study, ZnO films were prepared by using spray pyrolysis technique at different substrate temperatures and investigated the effect of substrate temperature on films morphological, structural, and optical properties.

2 Experimental

ZnO thin films were deposited onto soda-lime glass by spray pyrolysis method. The experimental homemade setup used for spraying process is given in Ref. [12]. The substrate temperatures were chosen to be 400, 450, 500, and 550 °C for investigating the effect of the substrate temperature on the physical properties of ZnO films. The substrate temperature was fixed during deposition and it was controlled within ± 10 °C by using a temperature controller unit kept on the metallic hot plate surface. The spray solution was prepared from 0.3 mol/L zinc chloride (Merck) solution in a mixture of deionized water and methanol with the ratio of 1:2 in exactly 60 mL for all of the films. A few drops of HCl were added to the solution in order to prevent the formation of zinc hydroxide. Compressed ambient air, which was supplied by an air compressor, was used to atomize the solution [15]. The nozzle-substrate distance was maintained at 28 cm.

The structure of ZnO films was investigated by X-ray diffraction (XRD) system (D8 ADVANCE, Bruker) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$ Å). Surface morphology was examined by a Hitachi S-4166 model field emission scanning electron microscope (FESEM). The thickness of the films was measured by FESEM. The optical transmittance spectrum of the films referenced to the glass was carried out in the wavelength range of 300–800 nm by a high resolution spectrophotometer (Ocean Optics HR4000CG-UV-NIR). Photoluminescence (PL) spectra were measured at room temperature using Cary Eclipse by a source with excitation wavelength of 320 nm. The electrical properties were evaluated by two-probe measurement.

3 Results and Discussion

3.1 Structural Properties

Figure 1 shows the XRD patterns of ZnO films prepared at different substrate temperatures. It reveals that all films are polycrystalline with Wurtzite crystal structure. The (002) plane is preferential orientation in all films. Very weak

Fig. 1 XRD patterns of ZnO films prepared at different substrate temperatures

Table 1 Structural parameters of ZnO films prepared at different substrate temperatures

Substrate temperature (°C)	Lattice constants (Å)		Diameter of rods (nm)	Length of rods (nm)
	<i>a</i>	<i>c</i>		
400	3.253	5.204	–	–
450	3.253	5.202	–	–
500	3.254	5.203	350–500	550–700
550	3.248	5.200	250–350	1,000–1,200

The coordinate *a* and *c* cited from JCPDS card of bulk Wurtzite ZnO are 3.250 and 5.207 Å, respectively

secondary peaks of (101), (102), (103), and (200) planes are observed at all substrate temperatures, and weak secondary peak of (100) plane is observed at 450 °C and higher substrate temperatures. These diffraction peaks are in good agreement with 36-1451 JCPDS card. These results suggest that the samples are highly crystallized Wurtzite ZnO with preferable *c*-axis orientation. Krunk et al. [13] and Alver et al. [14] also have reported (002) plane as a preferential direction. ZnO usually grows along the (002) orientation due to the lowest surface energy of (002) plane [16].

The lattice constants of ZnO films with different substrate temperatures are found by using the following equation [17]:

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2},$$

where *d* is the interplanar spacing; *h*, *k*, *l* are the indices of crystallographic plane; *a* and *c* are the lattice constants.

Fig. 2 Top view FESEM of ZnO films prepared at different substrate temperatures: **a** 400 °C; **b** 450 °C; **c** 500 °C; **d** 550 °C

The calculated lattice constants are in good agreement with JCPDS card, as shown in Table 1. The ratios of lattice constants (c/a) are about 1.60 for all substrate temperatures which are in good consistent with values of bulk Wurtzite ZnO.

The changes of morphology with substrate temperature by FESEM are shown in Figs. 2 and 3. At 400 °C ZnO film consists of grains with size of 200–450 nm. By increasing temperature to 450 °C, ZnO film exhibits more uniformly oriented grains with larger size of 350–500 nm. At high deposition temperature (450 °C), the formation of islands on the substrate are much bigger and fewer, but at low temperature, the high density and small islands form on the substrate and this is a well-known source of strain release [18]. The thicknesses of the films prepared at 400, 450, 500, and 550 °C are about 900, 850, 700, and 1,100 nm, respectively. As it can be seen from Fig. 2c, hexagonal rods start to grow at 500 °C. The regular hexagonal column rods are almost perpendicular to substrate, indicating that ZnO rods preferentially grow along the (002) direction. The diameter and length of the rods are 350–500 and 550–700 nm, respectively. At 550 °C, film is denser and consists of thinner rods. The diameter and length of the rods are 250–350 and 1,000–1,200 nm, respectively. It seems that increasing temperature (550 °C) leads to form smaller and denser islands on the substrate and therefore increasing the length of the rods instead of their diameter.

Krunk et al. [13] also synthesized ZnO rods by a simple pneumatic spray pyrolysis deposition technique in the temperature range of 490–560 °C. They reported that the temperature was a key factor for the formation of the ZnO microrods. Alver et al. [14] also reported that formation of ZnO rods started at around 400 °C by spray pyrolysis technique. They reported that the diameters of the hexagonal ZnO rods are getting bigger as the substrate temperature increases. Our results show that the formation of ZnO rods started at 500 °C and despite of their results, the rods diameter decreases with increasing substrate temperature.

3.2 Optical Properties

Figure 4 shows the optical transmission spectra of ZnO films deposited at different substrate temperatures, it reveals that the transmission of the films in visible range decreases with increasing substrate temperature. Maximum transmission in visible range is about 70% for ZnO film deposited at 400 °C and it decreases by about 10% for ZnO film deposited at 550 °C. The absorption edges of the films are observed in the range of 370–380 nm which correspond to the transition from valence band to conduction band. Decreasing in transmission can be explained by the observed changes in morphology. Increasing light scattering at the grain boundaries and higher substrate coverage at

Fig. 3 Cross-sectional FESEM images of ZnO films prepared at different substrate temperatures: **a** 500 °C; **b** 550 °C

Fig. 4 Optical transmission spectra of the ZnO films prepared at different substrate temperatures

450 °C leads to the decrease in optical transmission. Formation of ZnO rods above 500 °C leads to hazy films and decreases optical transmission. In addition, more thickness and higher substrate coverage lead to the decrease in optical transmission at 550 °C. At temperatures above 500 °C, penetrating of ions from soda-lime glass substrate to ZnO films and acting as a scattering center can also decrease the optical transmission. Similar results were obtained by Krunks *et al.* [13] but some literatures reported increasing in transmission with increasing in substrate temperature [14, 19].

In order to estimate the band gap, the absorption coefficient α was calculated. For the direct transition, the optical band gap energy of ZnO film was determined using the following equation [20]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

where E_g is the optical band gap energy, A and $h\nu$ are constants. The linearity of the plot of $(\alpha h\nu)^2$ versus $h\nu$ indicates a direct transition [21]. The extrapolated values of E_g are 3.37, 3.22, 3.21, and 3.19 eV for ZnO films produced using 0.1, 0.2, 0.3, and 0.4 mol/L precursor concentration, respectively.

The room temperature photoluminescence (PL) spectra of ZnO films prepared at different substrate temperatures are illustrated in Fig. 5. The figure shows a high-intensity UV peak around 380 nm (3.26 eV) and two peak emissions at ~ 440 nm (2.82 eV) and ~ 523 nm (2.37 eV) in blue and green regions, respectively. The UV emission corresponds to the band gap of ZnO material according to Dong *et al.* [22]; this UV emission is assigned to the recombination of bound excitons of ZnO. There is also a shoulder at UV peak at about 3.18 eV which may attribute to the neutral-donor-bound-exciton (D^0X) emission [23]. The origin of the visible emissions has not been conclusively established, and there have been a number of hypotheses proposed for each emission band [24]. The blue emission peak around 440 nm (2.82 eV) corresponds to the electron transition from the interstitial Zn to the top of the valence band [25]. The green PL emission band is assigned to the oxygen vacancies in ZnO [26]. This luminescence is due to the recombination of photogenerated hole with singly ionized oxygen vacancies. The visible peaks intensity decreases with increasing substrate temperature which shows the oxygen vacancies decrease at higher temperature. As previously mentioned, the increase of resistivity is due to chemisorption of oxygen at higher temperature. So, the decrease in the visible emission is expected.

3.3 Electrical Properties

The resistivity of ZnO films at 400, 450, and 500 °C are measured 40.6, 11.8, and 33.6 Ω cm, respectively. The

Fig. 5 PL spectra for ZnO films prepared at different substrate temperatures with the excitation wavelength of 325 nm

resistivity of ZnO film at 550 °C is too high to obtain. The reason for the changes in resistivity can be attributed to the surface morphology. Decreasing in resistivity at 450 °C is due to the increase in the grain size which leads to reduce electron scattering from the grain boundaries results in decreasing resistivity [27]. The resistivities of ZnO films consist of the rods are higher and the reduction of the rod diameter at 550 °C significantly leads to increase in resistivity. The higher resistivity at 500 and 550 °C can be attributed to surface states scattering. Also, after trapping the mobile carriers, the traps become electrically charged, creating a potential energy barrier, which prevents the motion of the carriers from one crystallite to other resulting in reducing their mobility and then resistivity [28]. The high resistivity also can be due to chemisorption of oxygen [29] at the grain boundaries. ZnO rods are separated from each other which cause the diffusing oxygen gas more readily into the rods grain boundaries. Therefore, the increase in the amount of adsorbed oxygen at the grain boundaries results in increasing resistivity in ZnO films consist of rods.

4 Conclusions

In this study, ZnO thin films are prepared at different substrate temperatures by spray pyrolysis technique. ZnO films comprising hexagonal elongated rods are grown above 500 °C. The XRD patterns exhibit the polycrystalline films with hexagonal structure. The preferred orientation in ZnO films is (002) plane. FESEM images show that the diameter of the rods decreases with increasing substrate temperature. The resistivity of ZnO rod films is

higher than ZnO films consisting of grains. The resistivity increases with increasing substrate temperature to 550 °C in ZnO rod film. Optical transmission of films decreases with the increase in substrate temperature. A UV emission at 3.21 eV due to exciton recombination and two visible emissions at 2.88 and 2.37 eV which can be attributed to defect emission in ZnO structure have been observed by PL spectra at room temperature.

References

- [1] C.W. Bunn, Proc. Phys. Soc. **47**, 835 (1935)
- [2] M. Rajabi, R.S. Dariani, A. Irajizad, F. Zahedi, Solid State Electron. **80**, 33 (2013)
- [3] N. Beermann, L. Vayssieres, S.E. Lindquist, A. Hagfeldt, J. Electrochem. Soc. **147**, 2456 (2000)
- [4] T. Soga, *Nanostructured Materials for Solar Energy Conversion* (Elsevier, Amsterdam, 2006)
- [5] L. Schlur, A. Carton, P. Leveque, D. Guillon, G. Pourroy, J. Phys. Chem. C **117**, 2993 (2013)
- [6] N.H. Alvi, W. Hassan, B. Farooq, O. Nur, M. Willander, Mater. Lett. **106**, 158 (2013)
- [7] M. Rajabi, R.S. Dariani, A.I. Zad, J. Alloys Compd. **509**, 4295 (2011)
- [8] A.N. Giorgobiani, A.N. Kozintsev, V.I. Kozlovskii, Z.I. Mako-vei, A.N. Redkin, Y.K. Skasyrskii, Inorg. Mater. **42**, 750 (2006)
- [9] R. Zhang, L.L. Kerr, J. Solid State Chem. **180**, 988 (2007)
- [10] P. Nunes, E. Fortunato, P. Tonello, F. Braz, Fernandes, P. Vi-larinho, R. Martins. Vacuum **64**, 281 (2002)
- [11] N. Audebrand, J.P. Auffredic, D. Louer, Chem. Mater. **10**, 2450 (1998)
- [12] F. Zahedi, R.S. Dariani, Thin Solid Films **520**, 2132 (2012)
- [13] M. Krunk, T. Dedova, I.O. Acik, Thin Solid Films **515**, 1157 (2006)
- [14] U. Alver, T. Kilinc, E. Bacaksiz, S. Nezir, Mater. Chem. Phys. **106**, 227 (2007)
- [15] P.S. Patil, Mater. Chem. Phys. **59**, 185 (1999)
- [16] H.Z. Zhang, X.C. Sun, R.M. Wang, D.P. Yu, J. Cryst. Growth **269**, 464 (2004)
- [17] B.D. Cullity, S.R. Stock, *Elements of X-Ray Diffraction* (Prentice Hall, New Jersey, 2001)
- [18] A. Avisou, C. Dufour, K. Dumesnil, D. Pierre, J. Cryst. Growth **297**, 239 (2006)
- [19] A. Mosbah, A. Maustaghfir, S. Abed, N. Bouhssira, M.S. Aida, E. Tomasella, M. Jacquet, Surf. Coat. Technol. **200**, 293 (2005)
- [20] D.K. Schroder, *Semiconductor Material and Device Characterization* (Wiley, New York, 1998)
- [21] U. Alver, T. Kılınç, E. Bacaksız, T. Küçükömeroğlu, S. Nezir, İ.H. Mutlu, F. Aslan, Thin Solid Films **515**, 3448 (2007)
- [22] L. Dong, Y.C. Liu, Y.H. Tong, Z.Y. Xiao, J. Colloid Interf. Sci. **283**, 380 (2005)
- [23] B.Z. Dong, G.J. Fang, J.F. Wang, W.J. Guan, X.Z. Zhao, J. Appl. Phys. **101**, 033713 (2007)
- [24] A.B. Djuricic, Y.H. Leung, Small **2**, 944 (2006)
- [25] B. Huang, G. He, H. Yang, Phys. B **405**, 4101 (2010)
- [26] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, J. Appl. Phys. **79**, 7983 (1996)
- [27] S. Mridha, D. Basak, Mater. Res. Bull. **42**, 875 (2007)
- [28] D.H. Tassis, C.A. Dimitriadis, J. Brini, G. Kamarinos, A. Birbas, J. Appl. Phys. **85**, 4091 (1999)
- [29] S.C. Chang, J. Vac. Sci. Technol. **17**, 366 (1980)