Effect of Annealing Temperatures and Pre-Heating on the Characteristics of a Nanocrystalline ZnO Thin Film Prepared by the Sol-Gel Dip-Coating Method

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For effectively fabricating nanocrystalline ZnO thin films by the sol-gel method, the relationships between the temperature of the heat treatment and the quality of the ZnO thin films was observed. The decomposition of the sol was analyzed by TG-DTA. The orientation of the *c*-axis of the ZnO thin film was identified by XRD. The morphology was observed and estimated by SEM. The experimental results did show that the orientation of the *c*-axis is determined by the pre-heating and annealing temperatures, and that the grain size and roughness of the ZnO thin films are mainly influenced by the annealing temperature. A qualified ZnO thin film was prepared by using a sol-gel with a pre-heating temperature of 275 °C for 10 min and an annealing temperature of 550 °C for 60 min.

Key words: Zinc Oxide; Dip-Coating; Microstructure.

1. Introduction

Zinc oxide is a wide band gap II-VI semiconductor with a potential application for transparent thin-film transistors, optical-electrical field such as ultraviolet light emitting diodes, UV photodetectors, and gas sensors [1 – 8]. In recent years various techniques such as sol-gel, spray pyrolysis, electrochemical deposition, chemical vapour deposition, magnetron sputtering, molecular beam epitaxy, vacuum arc technique, and radiofrequency had been developed to prepare ZnO thin films [9 – 14]. Recently there has been a growing interest in preparing ZnO thin films by the sol-gel method, which is simple, cheap, and deposits films with a large area and good uniformity of thickness [15 – 20]. More researches emphasised on preparing ZnO thin films with high conductivity and optical transmittance for solar cells by the sol-gel method [21 – 29]. The influence of the annealing temperature on the ZnO film quality has been investigated up to 800 °C for different deposition techniques. It has been found that a high quality ZnO film could be obtained at high substrate temperature [30 – 32]. However, from the viewpoint of device processing, it is desirable to grow high crystalline quality films at relatively low temperatures. Therefore, we prepared ZnO thin films for optical applications by using the sol-gel technology. The aim was to investigate the relation between the heat treatment temperatures (pre-heating temperature and annealing temperature) and the quality characteristics of the ZnO films. In this study we present the influence of the annealing temperature on the electrical and optical properties of undoped ZnO thin films grown on a glass substrate.

2. Experimental

All the chemicals were analytic grade reagents without further purification, purchased from Merck. To prepare a sol, 3.10 g zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], 0.86 g monoethanolamine (MEA) and adequate de-ionized water were added to 15 mL isopropanol, then heated to 65 °C with continuous stirring for 1 h. The coating substrate (microscope glass slide) was pre-heated at 275 °C for 10 min in air after each coating. The sol-gel coating was made usually 1 d after the sol was prepared, and the molar ratio of MEA to zinc acetate was maintained at 1 : 1.

Film deposition was carried out in air at room temperature by the dip-coating method onto the substrate with a controlled withdrawal speed of 1 cm min^{-1}. Then the films were annealed in a furnace at 350 °C, 450 °C, and 550 °C for 1 h. The precursor solution did not produce any precipitation after 60 d. The microscope glass slide (75 mm · 25 mm · 1 mm) cleaned

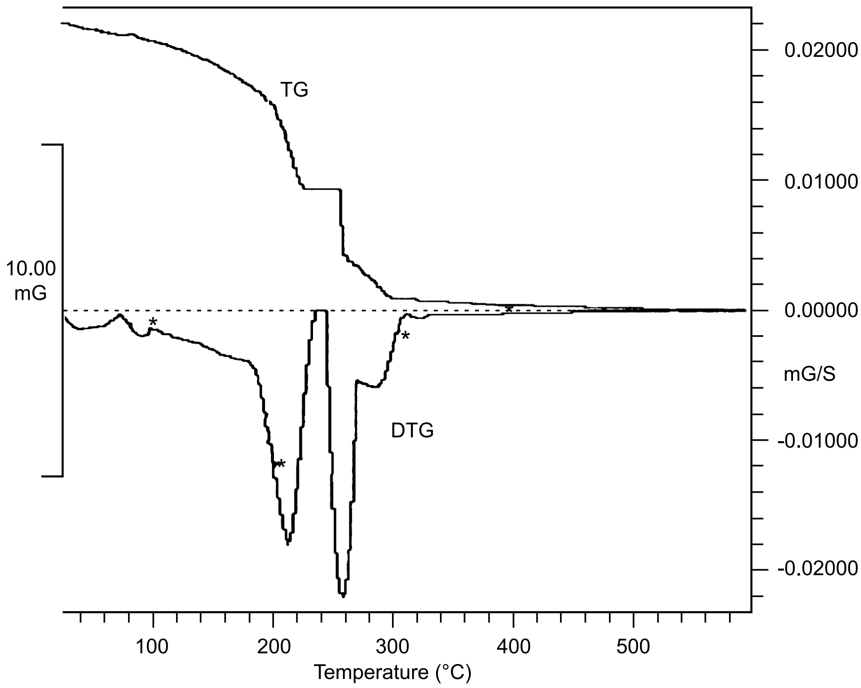

Fig. 1. TG-DTG curves of the dried gel.

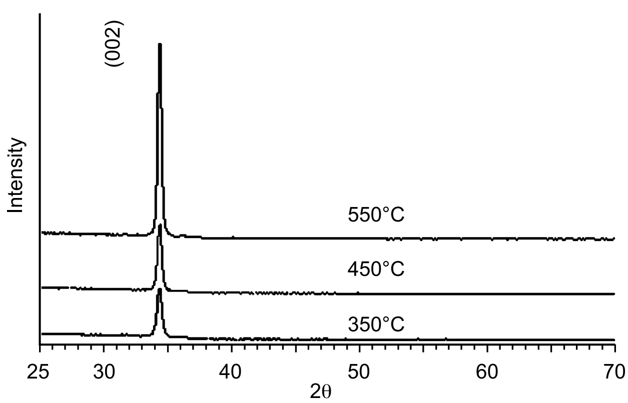

Fig. 2. XRD pattern of the ZnO thin film on a microscope glass slide by five dip-coatings (5-layer) pre-heated at 275 °C for 10 min and post-heated for 60 min at different temperature.

in dilute HCl solution and ethanol was used as substrate. After each coating, the films were pre-heated at 275 °C for 10 min, and post-heated at 350 °C, 450 °C, and 550 °C for 1 h. The deposition was repeated to obtain films with different thickness.

The thermal decomposition of the dried gel was examined by thermogravimetry-differential thermal analysis (TG-DTA; Mettler TG 5). The structure and crystalline size were determined by X-ray diffraction (XRD; Bruker D8 advanced X-ray diffractometer) with Cu K_α radiation and a scan rate of $0.03^\circ\ s^{-1}$. XRD showed wurtzite structure with [002] orientation. The transparency of the films was measured by a ultraviolet-visible spectrophotometer (CECIL-CE7500). The surface of the films was observed by scanning electron microscopy (SEM) with a Philips XL30 microscope.

3. Results and Discussion

Figure 1 shows TG-DTG curves of the dried gel. The exothermic peaking at 210 °C suggests the decomposition of the zinc precursor. The peak at 250 °C results from the formation of ZnO wurtzite crystals [33].

Figure 2 shows the XRD patterns of the ZnO thin film on glass, pre-heated at 275 °C and annealed at

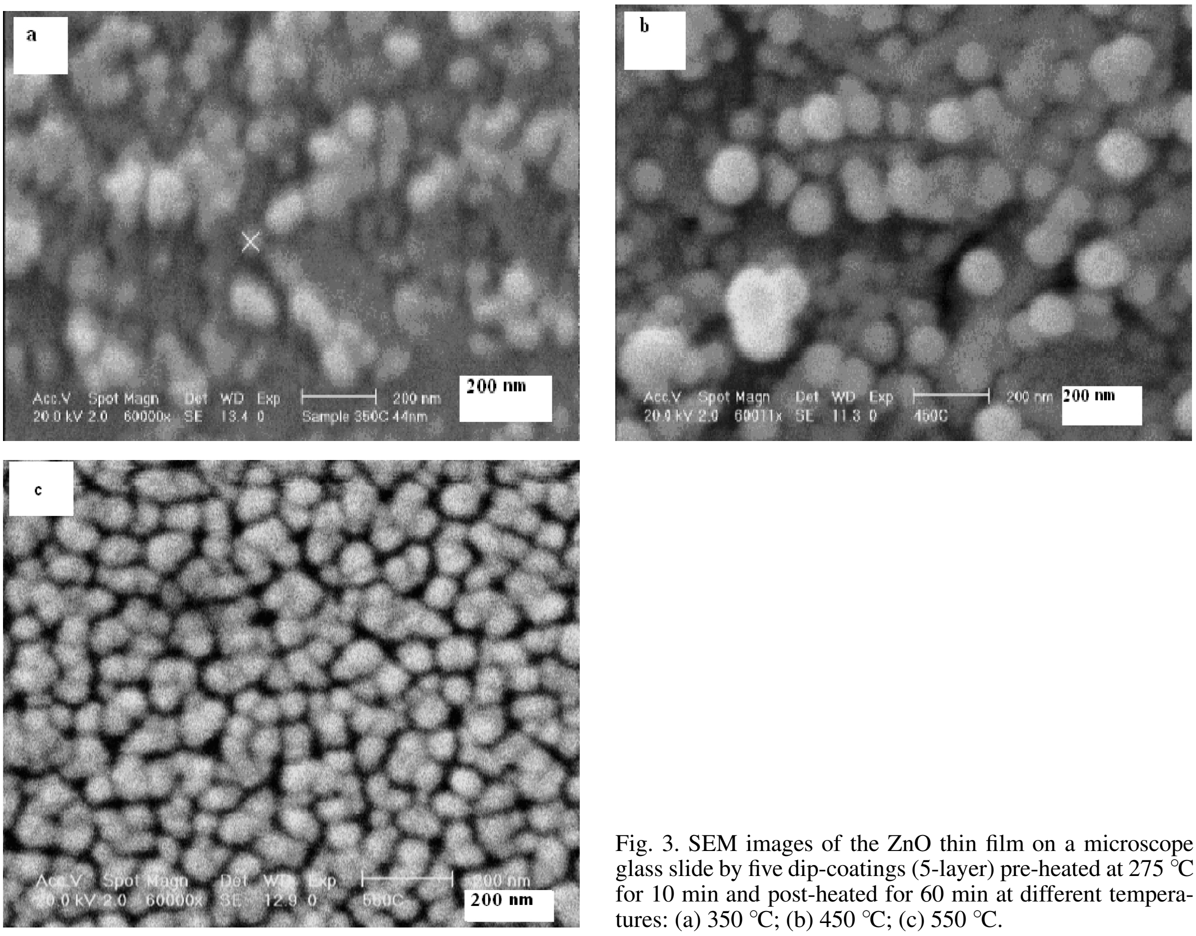

Fig. 3. SEM images of the ZnO thin film on a microscope glass slide by five dip-coatings (5-layer) pre-heated at 275 °C for 10 min and post-heated for 60 min at different temperatures: (a) 350 °C; (b) 450 °C; (c) 550 °C.

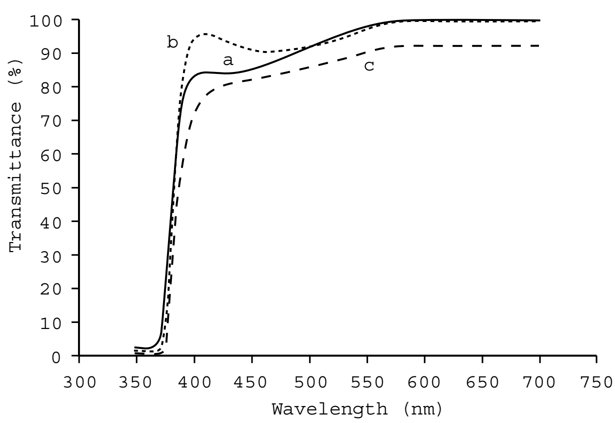

Fig. 4. Optical transmittance of ZnO thin films (5-layer) post-heated at various temperatures: (a) 350 °C; (b) 450 °C; (c) 550 °C.

350 °C, 450 °C, and 550 °C, respectively. The results clearly show that [002] orientation is preferred when the ZnO films are annealed at 550 °C. The preferred *c*-axis orientation is reported by Wang et al. [34], when the ZnO thin film is annealed at 800 °C. Comparing the XRD patterns of the thin films with ZnO powder showed that thin films have lower intensity and higher FWHM (fully width at half maximum) than the pow-

der, and the films are predominantly [002] oriented; finally films are crystallized at 550 ℃ with highest intensity. When the pre-heating temperature increases from 100 ℃ to 200 ℃ and 275 ℃, the annealing temperature, by which ZnO thin films were annealed to get a preferred *c*-axis orientation, increases from 300 ℃ to 400 ℃ and reaches highest at 550 ℃.

Figure 3 shows the SEM images of the nanocrystalline ZnO thin film. The average crystalline size of ZnO in the films annealed at 350 ℃, 450 ℃ and 550 ℃ are about 19, 22 and 24 nm, respectively. Also the average size of nanocrystalline ZnO thin films with various times of dip-coating post-heated at 550 ℃ is about 25 nm.

The optical transmittance of ZnO thin films preheated at 275 ℃ and post-heated at various temperatures, 350 ℃, 450 ℃, and 550 ℃, for 1 h are shown in Figure 4. The absorption at about 375 nm corresponds to an electronic transition beyond the band gap, 3.2 eV, of the crystalline ZnO. An increase in the transmittance of ZnO thin film is observed after the annealing treatment due to the release of hydroxide species remaining in the film. These results show that the sol-gel deposited ZnO films have potential application as transparent electrodes in optoelectronic devices.

4. Conclusion

ZnO thin films with highest preferred *c*-axis orientation, high optical transmittance and dense surface have been prepared on glass using the sol-gel method by pre-heating at 275 ℃ for 10 min and annealing at 550 ℃ for 60 min. The effects of the heat treatment (pre-heating temperature and annealing temperature) on the quality characteristics of the ZnO thin films were studied: The pre-heating and annealing temperatures influence the preferred [002] orientation, grain size and optical transmittance of ZnO films.

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[1] H.-S. Kang, S.-S. Pang, J.-W. Kim, G.-H. Kim, J.-H. Kim, S.-Y. Lee, Y. Li, H. Wang, and Q. X. Jia, Superlattices Microstruct. **40**, 501 (2006).
[2] B. N. Mukashev, A. B. Aimagambetov, D. M. Mukhamedshina, N. B. Beisenkhanov, K. A. Mit', I. V. Valitova, and E. A. Dmitrieva, Superlattices Microstruct. **42**, 103 (2007).
[3] A. G. Rolo, J. Ayres de Campos, T. Viseu, T. de Lacerda-Aroso, and M. F. Cerqueira, Superlattices Microstruct. **42**, 265 (2007).
[4] K. Grasza, E. Łusakowskaa, P. Skupinskia, H. Sakowskab, and A. Mycielskia, Superlattices Microstruct. **42**, 290 (2007).
[5] K. Nomura, A. Takagi, T. Kamiya, H. Ohta, M. Hirano, and H. Hosono, Jpn. J. Appl. Phys. **45**, 4303 (2006).
[6] D. S. Liu, C. Y. Wu, C. S. Sheu, F. C. Tsai, and C. H. Li, Jpn. J. Appl. Phys. **45**, 3531 (2006).
[7] S. J. Jiao, Z. Z. Zhang, Y. M. Lu, D. Z. Shen, B. Yao, J. Y. Zhang, B. H. Li, D. X. Zhao, X. W. Fan, and Z. K. Tang, Appl. Phys. Lett. **88**, 31911 (2006).
[8] S. Christoulakis, M. Suchea, E. Koudoumas, M. Katharakis, N. Katsarakis, and G. Kiriakidis, Appl. Surf. Sci. **252**, 5351 (2006).
[9] Y. F. Gao, M. Nagai, Y. Masuda, F. Sato, and K. Koumoto, J. Cryst. Growth **286**, 445 (2006).
[10] J. Y. Zhang, H. B. Feng, W. C. Hao, and T. M. Wang, J. Sol-Gel Sci. Technol. **39**, 37 (2006).
[11] J. N. Dai, H. B. Su, L. Wang, Y. Pu, W. Q. Fang, and F. Y. Jiang, J. Cryst. Growth **290**, 426 (2006).
[12] M. A. Lucio-Lopez, M. A. Luna-Arias, A. Maldonado, M. D. Olvera, and D. R. Acosta, Sol. Energy Mater. Sol. Cells **90**, 733 (2006).
[13] W. C. T. Lee, P. Miller, R. J. Reeves, and S. M. Durbin, J. Vac. Sci. Technol. B **24**, 1514 (2006).
[14] C. T. Yang, Z. Y. Zeng, Z. Chen, J. S. Liu, and S. R. Zhang, J. Cryst. Growth **293**, 299 (2006).
[15] Y. Sun, G. M. Fuge, and M. N. R. Ashfold, Superlattices Microstruct. **39**, 33 (2006).
[16] S. Fujihara, C. Sasaki, and T. Kimura, Appl. Surf. Sci. **180**, 341 (2001).
[17] B. Pal and M. Sharon, Mater. Chem. Phys. **76**, 82 (2002).
[18] Y. Q. Huang, M. D. Liu, Z. Li, Y. K. Zeng, and S. B. Liu, Mater. Sci. Eng. B **97**, 111 (2003).
[19] M. H. Aslan, A. Y. Oral, E. Mensur, A. Gul, and E. Basaran, Sol. Energy Mater. Sol. Cells **82**, 543 (2004).
[20] S. Q. Chen, J. Zhang, X. Feng, X. H. Wang, L. Q. Luo, Y. L. Shi, Q. S. Xue, C. Wang, J. Z. Zhu, and Z. Q. Zhu, Appl. Surf. Sci. **241**, 384 (2005).
[21] Y. Natsume and H. Sakata, Mater. Chem. Phys. **78**, 170 (2002).
[22] L. Znaidi, G. J. A. A. Soler Illia, S. Benyahia, C. Sanchez, and A. V. Kanaev, Thin Solid Films **428**, 257 (2003).
[23] V. Musat, B. Teixeira, E. Fortunato, R. C. C. Monteiro, and P. Vilarinho, Surf. Coat. Technol. **180**, 659 (2004).

[24] G. G. Valle, P. Hammer, S. H. Pulcinelli, and C. V. Santilli, J. Eur. Ceram. Soc. **24**, 1009 (2004).

[25] J. H. Lee, K. H. Ko, and B. O. Park, J. Cryst. Growth **247**, 119 (2003).

[26] K. Yoshino, T. Hata, T. Kakeno, H. Komaki, M. Yoneta, Y. Akaki, and T. Ikari, Phys. Status Solidi **2**, 626 (2003).

[27] R. Brenier and L. Ortega, J. Sol-Gel Sci. Technol. **29**, 137 (2004).

[28] A. Yamamoto, S. Atsuta, and Y. Kanemitsu, Physica E **26**, 96 (2005).

[29] X. L. Cheng, H. Zhao, L. H. Huo, S. Gao, and J. G. Zhao, Sens. Actuators B **102**, 248 (2004).

[30] B. P. Zhang, K. Wakatsuki, N. T. Binh, N. Usami, and Y. Segawa, Appl. Phys. Lett. **84**, 4098 (2004).

[31] W. I. Park, S. J. An, G. C. Yi, and H. M. Jang, J. Mater. Res. **16**, 1358 (2001).

[32] C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, Y. Lu, M. Wraback, and H. Shen, J. Appl. Phys. **85**, 2595 (1999).

[33] S. Bandyopadhyay, G. K. Paul, R. Roy, S. K. Sen, and S. Sen, Mater. Chem. Phys. **74**, 83 (2002).

[34] M. Wang, J. Wang, W. Chenc, Y. Cui, and L. Wang, Mater. Chem. Phys. **97**, 219 (2006).