

**CERAMICS**INTERNATIONAL

Ceramics International 33 (2007) 505-507

www.elsevier.com/locate/ceramint

# Short communication

# Electrostatic spray deposited ZnO thin films

Kyu-Seog Hwang <sup>a</sup>, Ju-Hyun Jeong <sup>a,b</sup>, Young-Sun Jeon <sup>a,b</sup>, Kyung-Ok Jeon <sup>a,b</sup>, Byung-Hoon Kim <sup>b,\*</sup>

<sup>a</sup>Department of Applied Optics and Institute of Photoelectronic Technology, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, South Korea

Received 17 August 2005; received in revised form 21 September 2005; accepted 18 October 2005 Available online 24 January 2006

#### **Abstract**

Transparent (>80% transmittance) ZnO thin films were prepared by electrostatic spray deposition for 100 min at 300 and 400 °C on soda—lime—silica slide glass substrates. X-ray diffraction analysis exhibited presence of poorly crystallized zinc oxide. Surface morphology of the films varied with the deposition temperature. The band gap values of the ZnO films deposited at 300 and 400 °C are 3.28 and 3.24 eV, respectively. © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: ZnO thin film; Electrostatic spray deposition; Surface morphology; Transmittance

### 1. Introduction

As a wide band gap material, ZnO has received increasing attention due to its possible application in ultraviolet (UV) light-emitting devices, electron-acoustic devices, UV detectors, and others [1–4]. Several techniques are being used to produce ZnO films, e.g., chemical vapor deposition, molecular beam epitaxy, radio frequency magnetron sputtering, and the sol–gel process [5–8].

Compared with other techniques, electrostatic spray deposition (ESD) [9–11] offers attractive advantages of easy control of composition and substrate temperature, high film growth rate, simple setup, low cost, and suitability for thick film preparation.

Here, we present the results of ZnO thin films prepared by ESD. Crystallinity, surface morphology, transmittance in the visible spectra range, and energy band gaps of the coated films was investigated.

# 2. Experimental procedure

A homogeneous precursor solution was prepared by mixing zinc acetate [(CH<sub>3</sub>COO)<sub>2</sub>Zn·2H<sub>2</sub>O] and 2-methoxyethanol (HOCH<sub>2</sub>OCH<sub>3</sub>). Since zinc acetate has a low solubility in 2-

methoxyethanol, 2-aminoethanol (H<sub>2</sub>HCH<sub>2</sub>CH<sub>2</sub>OH) (MEA) was added to obtain a clear solution (concentration: 0.6 mol zinc acetate/L 2-methoxyethanol). The molar ratio of MEA to zinc acetate was fixed at 1.0. The solution was stirred for 2 h to obtain homogeneity.

Deposition of ZnO films was performed using an ESD setup with a vertical configuration whose details have yet been reported [12]. A stainless steel needle (0.1 and 0.23 mm inner and outer diameter, respectively) was connected to a syringe pump (KD200, KD Scientific Inc., U.S.A.) using a silicon rubber tube. The flow rate of the precursor sol was kept at 0.2 mL/60 min. In order to obtain a stable cone-jet mode of electrostatic atomization, a high voltage (20 kV) was applied between the needle tip and the ground electrode by using a dc power supply (SHV120-30K-RD, Convertech Co. Ltd., Korea). Soda-lime-silica glass (SLSG) substrates cleaned in a H<sub>2</sub>O<sub>2</sub> solution, and rinsed in methanol were used. SLSG substrates on the ground electrode were heated at 300 and 400 °C for 100 min during spraying. A precursor solution was pumped through the nozzle which is placed 10 cm above the substrates.

The crystal structure of the coated films was characterized by high-resolution X-ray diffraction (HRXRD, X'pert PRO, Philips, Netherlands). The morphology of the films was examined by a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan). A scanning probe microscope (SPM, XE-200, PSIA, Korea) was used to analyze the surface roughness of the films. Transmittance in the visible

<sup>&</sup>lt;sup>b</sup> Department of Materials Science & Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, South Korea

<sup>\*</sup> Corresponding author. Tel.: +82 62 530 1711; fax: +82 62 530 1699. E-mail address: bhkim@chonnam.ac.kr (B.-H. Kim).

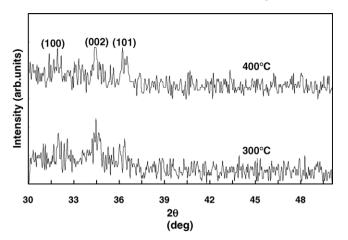


Fig. 1. XRD spectra of the ZnO films on SLSG substrates at 300 and at 400  $^{\circ}\mathrm{C}$  for 100 min

spectra region was analyzed by ultra violet (UV) spectro-photometer (Cary 500 Scan, Varian Co., Australia). The thickness of the annealed film was approximately 0.6  $\mu$ m, as determined by observation of the FE-SEM fracture cross-sections.

#### 3. Results and discussion

Fig. 1 shows XRD spectra of ZnO films deposited on SLSG substrates at 300 and 400 °C for 100 min. Broad diffraction peaks at (1 0 0), (0 0 2), and (1 0 1), possibly corresponding to poorly crystallized zinc oxide, were observed.

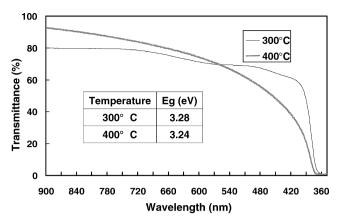


Fig. 3. Transmittance of the ZnO films on SLSG substrates 300 and at 400  $^{\circ}\mathrm{C}$  for 100 min.

Fig. 2 shows the FE-SEM images (a) and (b), and SPM images (c) and (d) of the ZnO thin films deposited at 300 and 400 °C. The ZnO thin films prepared at 400 °C by ESD showed a relatively smooth surface, while large particles were adsorbed on the surface of the film at 300 °C. With a decrease of deposition temperature from 400 to 300 °C, larger particles are found on the film surface. By decreasing the depositing temperature, the root mean square (RMS) roughness was increased to 109.2 nm. We assume that grain growth and large particles may be formed at decreased deposition temperature, resulting in higher RMS roughness.

Fig. 3 shows the transmission spectra of the ZnO films. All the films exhibit a high transmittance (>80%) in the visible

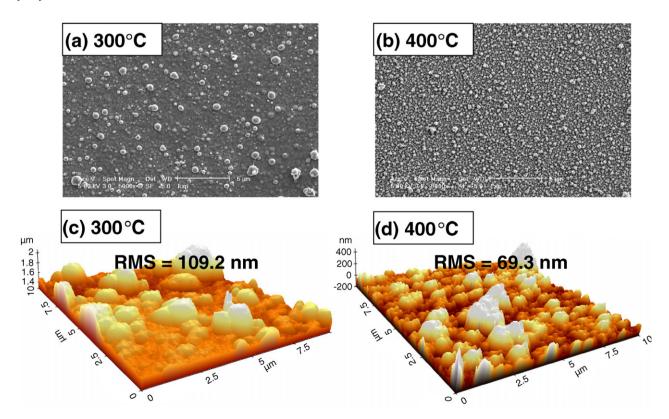


Fig. 2. FE-SEM images (a) and (b) and SPM images (c) and (d) of the ZnO films.

region, and show a sharp fundamental absorption edge at about 0.38–0.40  $\mu m$ , which is very close to the intrinsic band-gap of bulk ZnO. The transmittance is expected to depend on several factors, such as oxygen deficiency, surface roughness, and impurity centers [13]. We can assume that the lower transmittance of the film deposited at 300 °C is mainly due to the surface roughness of the film, as shown in Fig. 2.

Furthermore, we calculated the bandgap values of the films from their transmission spectra using the following equation [14]:

$$\alpha = (h\nu - E_{\rm g})^{1/2}$$

where  $\alpha$  is the absorption coefficient,  $E_{\rm g}$  is the band gap and  $h\nu$  is the photon energy. The intersection of the linear region on the  $h\nu$  axis of the plot of  $\alpha^2$  versus  $h\nu$  gives the band gap of the ZnO films deposited on SLSG substrates. As shown in Fig. 3, using this method the bandgap values of the ZnO films are found to be 3.28-3.24 eV.

## 4. Conclusions

Poorly crystallized ZnO films possessing high transmittance were deposited by ESD on SLSG substrates. With the decrease of deposition temperature from 400 to 300 °C, larger particles are found on the film surface. All the films exhibit a high

transmittance (>80%) in the visible region, and show a sharp fundamental absorption edge at about 0.38–0.40 µm.

## References

- [1] Y. Chen, H. Ko, S. Hong, T. Yao, Appl. Phys. Lett. 76 (5) (2000) 559-561.
- [2] Y. Chen, H. Ko, S. Hong, T. Yao, Y. Segawq, J. Cryst. Growth 214/215 (2000) 87–91.
- [3] A.B.M. Ashrafi, B. Zhang, N. Ninh, K. Wakatsuki, Y. Segawa, Jpn. J. Appl. Phys. 43 (2004) 1114–1117.
- [4] M. Chen, Z. Pei, X. Wang, C. Sun, L. Wen, J. Mater. Res. 16 (7) (2001) 2118–2123.
- [5] B. Zhao, H. Yang, G. Du, X. Fang, D. Liu, C. Gao, X. Liu, B. Xie, Semicond. Sci. Tech. 19 (2004) 770–773.
- [6] Y. Chen, S. Hong, H. Ko, M. Nakajima, T. Yao, Appl. Phys. Lett. 76 (2) (2000) 245–247.
- [7] C. Lin, C. Hsiao, S. Chen, S. Cheng, J. Electrochem. Soc. 151 (5) (2004) G285–G288.
- [8] D. Mondelaers, G. Vanhoyland, H. Rul, J. D'haen, M. Bael, J. Mullens, L. Pouche, J. Sol–Gel Sci. Tech. 26 (2003) 523–526.
- [9] K. Choy, Mater. Sci. Eng. C16 (2001) 139-145.
- [10] R. Chandrasekhar, K. Choy, Thin Solid Films 398-399 (2001) 59-64.
- [11] C. Chen, K. Varhaug, J. Schoonman, J. Mater. Syn. Proc. 4 (3) (1996) 189– 194
- [12] Y. Lim, B. Kim, Y. Jeon, K. Jeon, K. Hwang, J. Ceram. Proc. Res. 6 (3) (2005) 255–258.
- [13] V. Gupta, A. Mansingh, J. Appl. Phys. 80 (2) (1996) 1063-1073.
- [14] K. Hwang, Y. Jeon, B. Kang, K. Nishio, T. Tsuchiya, J. An, B. Kim, J. Kor. Phys. Soc. 46 (2) (2005) 521–526.