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Structural and Optical Properties of Reactive Sputtered ZnO Thin Films on Flexible-Transparent Substrates

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ABSTRACT

In this work, ZnO thin films with different thickness (100 nm and 50 nm) were deposited onto flexible-transparent substrates by high vacuum (HV) reactive direct current (DC) magnetron sputtering technique, using oxygen as a reactive gas. The structural and optical properties of the films were investigated by X-ray diffractometer (XRD), room temperature photoluminescence (PL) and UV–Vis spectrometer. The both obtained films had a hexagonal structure and a highly preferred orientation with the c-axis perpendicular to the substrate. The electronic transitions from the conduction band to the valence band (called as band gap) of the films was about 3.2 eV. It was observed that the exitonic transition energy of the films shifted blue emission with increasing the film thickness. In addition, the optical transmittances of the films were about 80 % in the visible region.

Keywords: ZnO, thin films, transparent, flexible, DC Sputtering

1. INTRODUCTION

ZnO thin films are important materials for new-technological applications due to the excellent properties such as wide optical band gap (3.37 eV), large exciton binding energy (60 meV), high radiation hardness, non-toxicity and high thermal and chemical stability. ZnO thin films with a large band gap are transparent to a visible light which can be widely used as an optical coating material in applications of ultraviolet light emitting diodes, lasers, sensor and solar cells [1-5]. Deposition of oxide based thin films on flexible-transparent substrates has become crucial for the some flexible electro-optical device fabrication. Thus, it can be obtained the light weight, small volume foldable and flexible devices. In literature, oxide based thin films have been deposited on various kinds of flexible substrates such as polyethylene terephthalate (PET) [6], poly carbonate (PC) [7], polyimide (PI) [8], polypropylene adipate (PPA) [9], polytetrafluoroethylene (Teflon) [10], and a composite materials (TPT) [11].

ZnO thin films can be deposited on flexible substrates by using several deposition techniques [6-10]. Among them, the sputtering is a preferred method due to its simplicity, low cost, the possibility of obtaining uniform films on the variety of the substrate at high or low growth temperature.

In this present work, ZnO thin films were deposited onto flexible-transparent substrates by high vacuum (HV)

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reactive direct current (DC) magnetron sputtering technique and influence of film thickness on the structural and optical properties of the films was investigated by x-ray diffractometer (XRD), room temperature photoluminescence (PL) and UV–Vis spectrometer, respectively.

2. EXPERIMENTAL

The ZnO thin films were deposited onto flexible acetate substrates by HV reactive DC magnetron sputtering system at room temperature. Before the deposition process, the substrates were cleaned ultrasonically in acetone and then alcohol and rinsed thoroughly in deionized water of resistivity of 18 MΩ-cm. High purity (%99,999) Zn target was used to obtain the ZnO thin films. The automatic control system of gas valves was used for Ar and O_2. The flow of Ar/O_2 in the chamber was maintained at 10/20. The films with the film thickness of 100 nm and 50 nm were named as N63 and N64, respectively. The constant pressure was kept at 6.3×10^{-3} mbar and the temperature of the substrates was maintained at room temperature. Thickness of the deposited films was measured by using a thickness meter in-situ.

After the deposition, the thickness of the films was measured with a stylus type profile meter. The structure and crystalline quality of the films were analyzed with x-ray diffractometer (D8 Discover, Bruker) by using CuKα_1 (1.540 Å) radiation. Optical band gap of the films were performed by room temperature PL measurements (HORIBA JobinYvon) by using a 50 mW HeCd laser (λ = 325 nm) which is an excitation light source. The optical transmittance measurements were performed by UV–Vis spectrometer (Lambda 2S, Perkin Elmer) at RT in the range of 200–1100 nm.

3. RESULTS AND DISCUSSIONS

Figure 1 shows XRD patterns of the reactive sputtered ZnO thin films on flexible-transparent substrates at 100 nm (N63) and 50 nm (N64) film thickness. The both obtained films exhibit a strong peak at 34.421° in the XRD spectrum correspond to the ZnO pattern from the JCPDS card No. 00-036-1451. This indicates that the films are successfully deposited on the substrates at the orientation of the wurtzite structure of the bulk ZnO (002) plane. As shown in this figure, the peak intensity of the sample N63 is higher than the other. In addition, the full wide of half maximum (FWHM) of the peaks for the N63 and N64 samples were calculated as 0.68° and 0.83°, respectively. In order to obtain the detailed structural properties, the grain size of the films was calculated from the FWHM values using the Scherrer's formula [12]. The grain size decreased from 21.10 nm to 17.28 nm and full width half of maximum (FWHM) increased from 0.68° to 0.83°, with decreasing the film thickness. These results suggest that the crystallization of the sample N63 was better than the sample N64.

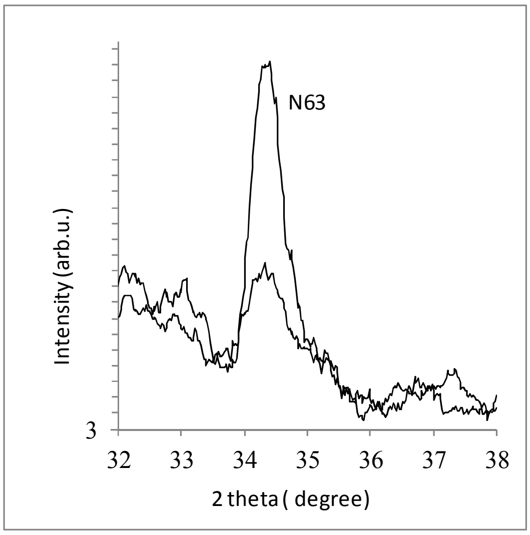


Figure 1. XRD pattern of the ZnO thin films on flexible-transparent acetate substrates

The PL emission spectra of the samples are shown in Figure 2. In this figure, three band maxima are labeled as A, B and C. The peak C corresponds to the electronic transitions from the conduction band to the valence band (called as band gap) of the films located at about 3.25 and 3.21 eV for N63 and N64 samples, respectively. The other peaks (A and B) can be attributed to the electronic transition originated from defect levels in the band gap region [13]. The broad band at located about 2.6 eV (peak A) can originate from oxygen vacancies which act active center in the PL emission. The other defect level at located about 3 eV (peak B) closed the band gap energy of ZnO may be related the reducing of Zn atoms as reported in the literature [13]. In addition, PL intensity of the sample N63 is higher than the sample N64.

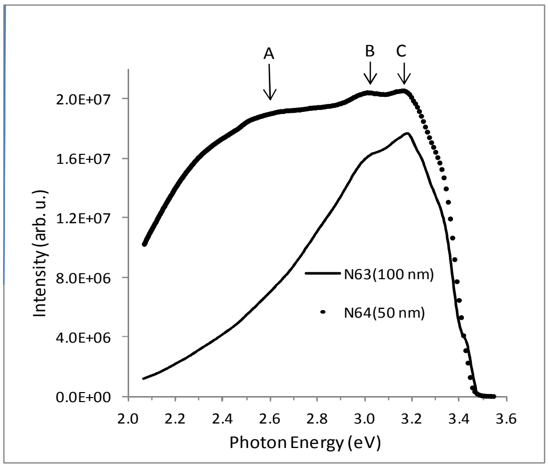
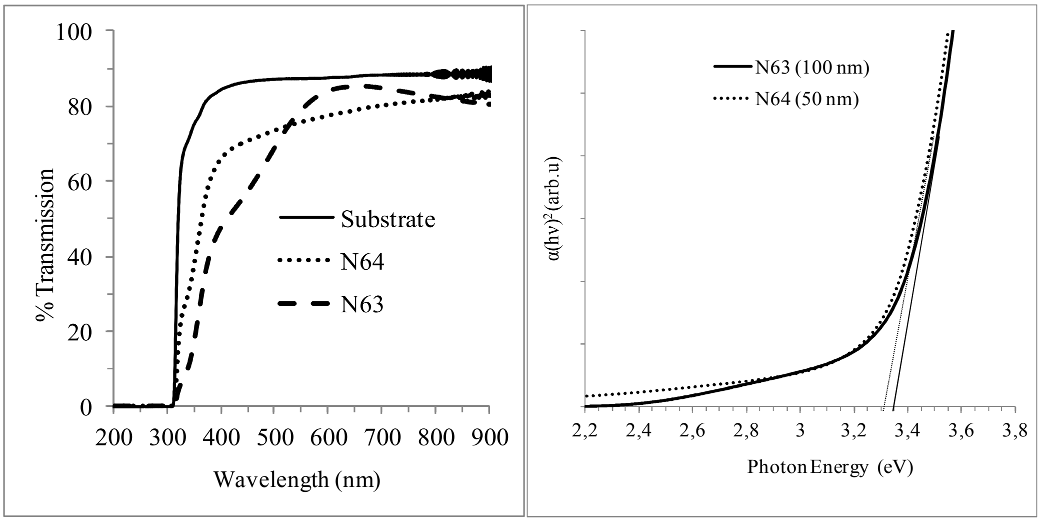


Figure 2. PL emission spectra of the ZnO thin films on flexible-transparent acetate substrates

Fig. 3a shows the transmittance spectra as a function of wavelength in the range from 200–1100 nm for the bare flexible-transparent acetate substrate and the reactive sputtered ZnO thin films on the substrates. From this figure, it was seen that the transmissions in the visible range of the ZnO thin films were about 80%. The high transmission in the structure of the ZnO films is transparent in visible region. The trend in the UV–Vis absorbance properties of the samples is shown in Fig. 3b.

The strong UV absorption was observed for both of the samples. The band gaps (E_g) of the samples were calculated by linear fitting to the linear region of the absorption spectra. The E_g values for the sample N63 and N64 were obtained as 3.29 and 3.26 eV, respectively, and was blue-shifted by increasing the film thickness of the ZnO thin films as similar the UV emission in the PL spectra.



(a) (b)

Figure 3. (a) Transmission spectra of the bare substrate and reactive sputtered films. (b) $\alpha(hv)^2$ versus photon energy for the deposited samples. Where, α is absorption coefficient.

4. CONCLUSION

The ZnO thin films were successfully deposited on the flexible-transparent acetate substrates by HV DC magnetron sputtering at room temperature. The film thickness dependence of the structural and optical properties of the obtained films was investigated. The XRD results revealed that deposition of the ZnO thin films in the wurtzite structure were successfully achieved on the flexible substrates. The optical transmissions in the visible range of the ZnO films were about 80%. 100 nm thick ZnO thin films have more transmission in the visible area, especially in 500-800 nm, is higher than the 50 nm thick ZnO thin films. The band gaps (E_g) of the samples became narrower with increasing the film thickness. In conclusion, the quality of the films is greatly affected by film thickness during deposition. We suggest that the ZnO thin films on the flexible substrates can be used as TCO films in opto-electronic devices such as thin film photovoltaics, flat panel displays and organic light emitting diodes.

ACKNOWLEDGEMENTS

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

[1] D. C. Kim, W. S. Han, H. K. Cho, B. H. Kong, H. S. Kim, Appl. Phys. Lett., 91(13), 231901 (2007).

[2] S. Bai, W. Wu, Y. Qin, N. Cui, D.J. Bayerl, X. Wang, Adv. Funct. Mater. 21, 4464–4469 (2011).

[3] A. Tsukazaki , A. Ohtomo , T. Onuma , M. Ohtani , T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma , M. Kawasaki , Nat. Mater., 4, 42 (2005).

[4] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, C. L. Lin, Appl. Phys. Lett., 84, 3654 (2004).

[5] M. Law, L. E. Greene, J. C. Johnson, R. Saykally , P. D. Yang, Nat. Mater., 4, 455 (2005).

[6] A. N. Banerjee, C. K. Ghosh, K. K. Chattopadhyay, M. Hideki, A. K. Sarkar, A. Akiba, A. Kamiya, T. Endo, Thin Solid Film, 496, 112-116 (2006).

[7] J. Lee, D. J. Lee, D. G. Lim, K. Yang, Thin Solid Film, 515, 6094–6098 (2007).

[8] X.-T. Hao, J. Ma, D. -H. Zhang, Y. -G. Yang, H. -L. Ma, C. -F. Cheng, X. -D. Liu, Mater. Sci. Eng. B, 90, 50–54 (2002).

[9] H. L. Ma, X. T. Hao, J. Ma, Y. G. Yang, S. L. Huang, F. Chen, Q. P. Wang, D. H. Zhang, Surf. Coat. Technol., 161, 58–61 (2002).

[10] Y. Y. Liu, Y. Z. Yuan, X. T. Gao, S. S. Yan, X. Z. Cao, G. X. Wei, Mater. Lett., 61, 4463–4465 (2007).

[11] X. -J. Wang, Q. -S. Lei, W. Xu, W. -L. Zhou, J. Yu, Materials Letters, 63, 1371–1373 (2009).

[12] H. P. Klug, L. E. Alexander, X-ray Diffraction Procedures (Wiley, New York, 1974).

[13] Z. Liang, X. Yu, B. Lei, P. Liu, W. Mai, Journal of Alloys and Compounds 509, 5437–5440 (2011).