Structural and Optical Properties of Undoped ZnO Thin Films Synthesized by Advanced Spray Pyrolysis with Different Thickness

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Abstract. *In this work, Zinc Oxide (ZnO) thin films were prepared onto glass at low substrate temperature by advanced spray pyrolysis technique. The effect of film thickness variation on microstructure, surface morphology and optical properties were investigated with X-ray diffractometry, UV–visible spectrophotometer and Photoluminescence (PL) spectroscopy, respectively. The crystallographic analyses confirm that all the samples have a wurtzite structure and are preferentially oriented along (002) direction. With the increase of film thickness, the crystalline quality of the films is gradually improved. The optical measurements show that all the samples have a strong transmission higher than 80% in the visible range. A slight shift of the absorption edge towards the large wavelengths was observed as the thickness increased. The photoluminescence (PL) studies on these films showed UV/ Violet photoluminescence (PL) band.*

Keywords: ZnO thin films, Thickness, Spray Pyrolysis, Optical.

INTRODUCTION

In recent years, ZnO have been the topic of much interest as it is a promising luminescent semiconductor material comparable to GaN on a number of properties, such as wurtzite structure and direct wide band-gap (GaN: 3.39 eV, ZnO: 3.37 eV at room temperature) [1]. To ensure the sustainable development of competent properties of ZnO in such optical devices, a form of thin film with high quality must be formed as a coating on the surface of the devices. Unlike a bulk material, the thin film properties are usually thickness dependent. This makes the film thickness more vital not only as a geometrical parameter but also as a functional parameter in design of materials and devices.

In this work, ZnO thin films are deposited at various thicknesses on glass at low substrate temperature by advanced spray pyrolysis technique and the dependence of structural and optical properties on the film thickness is investigated.

EXPERIMENTAL

The experimental setup of advanced spray pyrolysis technique and its other details have been reported elsewhere [2]. The precursor solution used was of 0.1M concentration of high purity zinc acetate dissolved in methanol. To study the thickness effect, only the spray solution quantity viz. 50, 100, 150, 200ml in order to obtain different thicknesses as follows: 135, 216, 298 and 392 nm. Different volumes of spraying solutions were atomized by compressed air onto preheated glass substrates maintained at 473K. During the course of spray, other parameters viz. nozzle to substrate distance (38cm), core temperature (598K), spray rate (~6ml/min), air pressure (10LPM) were essentially kept the same.

RESULTS AND DISCUSSION

X-ray Diffraction Studies

A typical X-ray diffraction pattern of the ZnO film of 298 nm thickness is shown in the inset of figure 1. The matching of observed and standard d-values revealed that all the films prepared are polycrystalline ZnO with hexagonal (wurtzite) crystal structure and patterns assure a preferential orientation along c-axis perpendicular to the substrate. In general, smaller the FWHM is, the higher is the film crystallinity. Further, it has been found that the film thickness plays an important role in determining the FWHM of ZnO thin films (see inset) and thereby their crystallinity. It is seen that the FWHM of the (002) diffraction peak decreases as the thickness increases becomes minimum for 298 nm film and again tends to increase for higher thickness. It means that the film quality i. e. crystallinity increases with increase of thickness (i.e.

growth rate) of ZnO films. The 298 nm ZnO film shows finest crystallinity amongst all films.

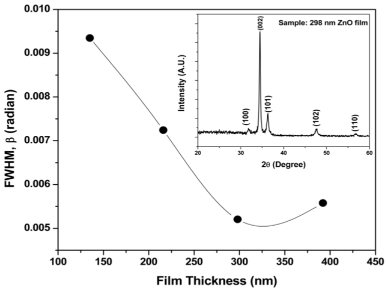

FIGURE 1. Evolution of the FWHM of ZnO thin film with its thickness. Inset shows a typical XRD pattern of ZnO film with 298 nm thickness.

Optical Absorption Studies

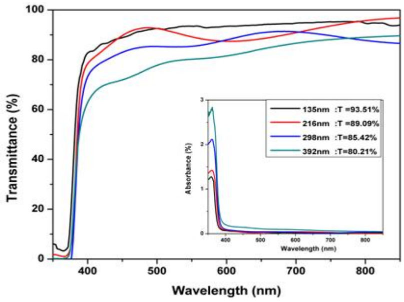

FIGURE 4. Optical transmittance spectra versus wavelength for ZnO thin films with different thickness. [Inset shows corresponding absorption spectra]

The effect of thickness on the optical transmittance and the band gap (E_g) values of the ZnO films have been studied. Figure 4 shows the transmittance spectrum as a function of the wavelength for the ZnO films with different thickness; the inset shows the optical absorption spectrum vs. wavelength. At 550 nm, the average transmittance of the films including substrates is over 80%. The transmission decreases sharply near low wavelength region due to the band gap absorption. With increase in film thickness, the transmittance of the films decreased due to the thickness and roughness effect. Additionally, a shift of the absorption edge proportional to the thickness values, towards UV energies is evident from the spectra. This blue shift of absorption edge may be ascribed to the difference in grain size [3]. Further, the optical energy band gap determined by using the Tauc's plot and band gap of the films observed to decrease from ~3.28 eV to ~3.27 eV as the thickness increased from 135 nm to 298nm.

Photoluminescence Spectra

Fig. 6 shows the room temperature PL spectra of the ZnO samples. Single Ultraviolet (UV) luminescence band have been observed along with much broad green emissions and UV emission intensity decreases with the increase in film thickness, becomes minimum for 298 nm film and again tends to increase for further thickness increase. According to the literature [4-6], the UV emission peak at around 3.13 eV is a near band edge (NBE) emission. At minimum thickness (i. e. 135 nm), the maximum intensity with narrowest full-width at half-maximum (FWHM) of UV emission peak was obtained (Inset of Figure 6).

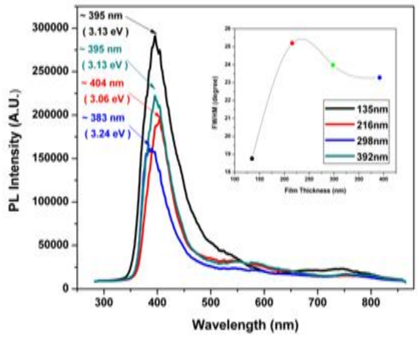

FIGURE 6. Room temperature photoluminescence spectra of ZnO thin films with different thicknesses. (Inset shows variation in FWHM of PL peak with film thickness.)

Conclusions

The ZnO thin films have been successfully deposited at low substrate temperature (~ 473K) using an advanced spray pyrolysis technique. The ZnO nanocrystallites had wurtzite crystal structures and increase in film thickness improves the crystal quality of the film. All films are highly exhibit average transmittance above 80% and the band gap was observed to exhibit a 'red shift' with an increasing film thickness. The PL analyses suggest a near band edge (NBE) emission peak resulting into strong UV emission. At lower film thickness results into the maximum intensity with narrowest full-width at half-maximum (FWHM) of UV emission peak.

REFERENCES

1. U. Ozgur, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkocd, J. Appl. Phys. 98 (2005) 041301.
2. P. S. Shewale, S. I. Patil, M. D. Uplane, Semicond. Sci. Technol. 25 (2010) 115008.
3. S.-S. Lin, J.-L. Huang, D.-F. Lii, Surface & Coatings Technology 190 (2005) 372.
4. F. Wu, L. Fang, Y.J. Pan, K. Zhou, H.B. Ruan, G.B. Liu, C.Y. Kong, Thin Solid Films 520 (2011) 703.
5. X.M. Zhang, W. Mai, Y. Zhang, Y. Ding, Z.L. Wang, Solid State Commu. 149 (2009) 293.
6. T. Kryshtab, V. S. Khomchenko, V. B. Khachatryan, N. N. Roshchina, J. A. Andraca-Adame, O. S. Lytvyn, V. I. Kushniren, J Mater Sci: Mater Electron 18 (2007) 1115.s