



Original Article

Fabrication and properties of nanocrystalline zinc oxide thin film prepared by sol-gel method

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Abstract

Zinc oxide (ZnO) thin films were prepared on glass substrate by sol-gel dip-coating method. The structural properties were investigated by x-ray diffraction (XRD) method and atomic force microscope (AFM). The optical properties were measured by UV-Vis spectrophotometer. The XRD patterns showed that the films formed preferred orientation along c-axis which increased as a function of polyvinyl pyrrolidone (PVP) concentration. The films gave the crystallite size of 15-18 nm calculated by Scherrer's formula and grain size of 48-70 nm measured by AFM at different PVP concentrations. The direct optical band gap of the films was in the range of 3.80-4.08 eV.

Keywords: ZnO, Sol-gel, PVP, Optical properties

1. Introduction

Zinc oxide (ZnO) is a wide band gap II-VI semiconductor which exhibits a hexagonal wurtzite structure. ZnO is one of the candidate materials for many applications due to its significant physical and chemical properties; for example, ZnO has been given much attention as a host material for transparent conducting film because impurity-doped ZnO films show high transparency above 90% in a visible region and low resistivity around 5×10^{-4} W.cm (Mahmood *et al.*, 1995). Also, ZnO has a large exciton binding energy of 60 meV at room temperature so ZnO provides prospects of practical lasers with low threshold even at high temperature (Weitao *et al.*, 2007). Moreover, ZnO can be used in other applications such as gas sensors (Sarala *et al.*, 2006), surface

acoustic wave devices (Leo *et al.*, 2006) and solar cells (Fay *et al.*, 2006). In the chemical research field, ZnO is well known as a photocatalyst with high chemical activity.

Nanotechnology has become one of the most interesting areas of scientific research in the past few years. The most attention area of nanotechnology receiving much attention is material research, including the synthesis, characterization and application of nano-meter-sized metals, semiconductors and ceramics. One reason for this attention is the nanomaterials have properties akin to the molecular and macroscopic levels. A great driving force for research in this field is their potential in new and improved properties and applications (Bozhko *et al.*, 2004). Major efforts in formation of thin film can be grouped into two broad areas: gas phase synthesis and sol-gel method. The sol-gel technique has gained worldwide interest because this technique offers several advantages such as its high chemical homogeneity, low processing temperature and the possibility of

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controlling the size and morphology of particles. An oxide network is obtained during process from metal molecular precursors through hydrolysis and subsequent condensation reactions. Several researchers have prepared the ZnO thin films via sol-gel dip coating for elucidating the structural, electrical and optical properties (Murali, 2007; Tianbao *et al.*, 2007; Zhifeng *et al.*, 2007) because this method can exclusively apply for the fabrication of oxide transparent multi-layers with a high degree of planarity and surface uniformity (Klein, 1988). Moreover, the dip coating is simplicity method and the film thickness and film quality can be controlled easily (Lopez *et al.*, 2003).

The aims of this report are to investigate the effect of PVP on structural and optical properties of deposited ZnO thin film via sol-gel dip-coating method.

2. Experimental procedure

Thin films of polymer-capped ZnO nanocrystalline were synthesized by sol-gel dip-coating method using polyvinyl pyrrolidone (PVP) with molecular weight of 8,000 as capping agent. The 0.2195 g of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was dissolved in 10 mL of ethanol and subsequent 90 mL of distilled water was dropped and finally PVP with amounts of 0.08, 0.24, 0.40, and 0.56 g were added into prepared $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution so as to maintain the mole ratio between PVP/ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ at 0.01, 0.03, 0.05, and 0.07, respectively. These solutions were continuously stirred for 24 hours at room temperature before using as starting sol in dip-coating process. In this study, the glass substrates were cleaned in a mixture solution of HCl and HNO_3 (1:2) for 10 min., they were then rinsed with distilled water and ethanol for several times and dried before dipping into starting sol. Each layers of as-prepared films were dried at 80°C in air for 15 min. The dipping process was conducted 5 times after each layer cooled down to room temperature. Finally, all films were calcined at 550°C in air for 1 hour to ensure that all organic species were expelled from the films.

The crystal structure of calcined films was examined by x-ray diffractometer (XRD, SEIFERT) in the 2θ range of 10-70 degree using $\text{CuK}\alpha$ radiation with wavelength (λ) of 0.15406 nm. Morphology and roughness were evaluated by atomic force microscope (AFM, Digital Instruments Nanoscope III) and optical transmission spectra of ZnO films were measured by UV-Vis spectrophotometer (UV-Vis, Shimadzu 3100) in the wavelength region of 200-2000 nm.

3. Results and discussion

3.1 Structural analysis

First of all, the dependence of PVP concentrations on crystallinity of ZnO thin films were investigated by XRD technique as shown in Figure 1. We found that PVP played as an important role in improvement of crystallinity and

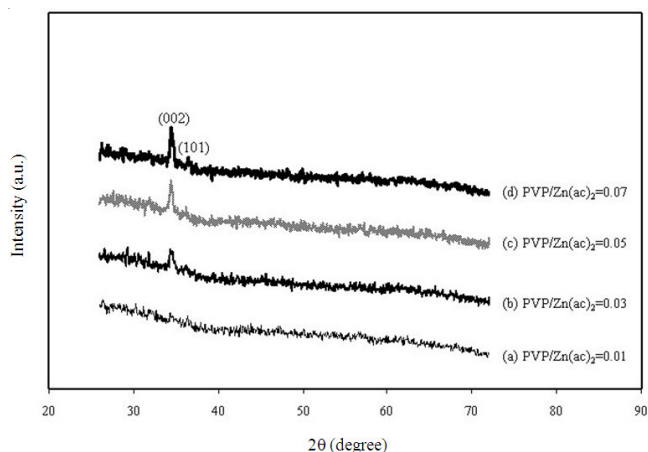


Figure 1. X-ray diffraction patterns of ZnO thin films at different mole ratios of $\text{PVP}/\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$.

also preferred orientation along the c-axis of the ZnO thin films due to PVP creating some hydroxyl ions (OH^-) when dissolving in solvent, which were observed as an increase of pH. These OH^- ions had promoted the hydrolysis reaction of zinc molecule with distilled water so the crystallite size of ZnO thin films increased according to an increase of PVP concentrations. However, the crystallite size is somewhat constant at PVP higher than 0.24 g. This can be explained by the ZnO nanoparticles being capped by PVP molecule at higher PVP concentrations so the growth of ZnO was inhibited (Casswell *et al.*, 2003). The crystallite size was calculated from Debye-Scherrer's formula (Khranovskyy *et al.*, 2006).

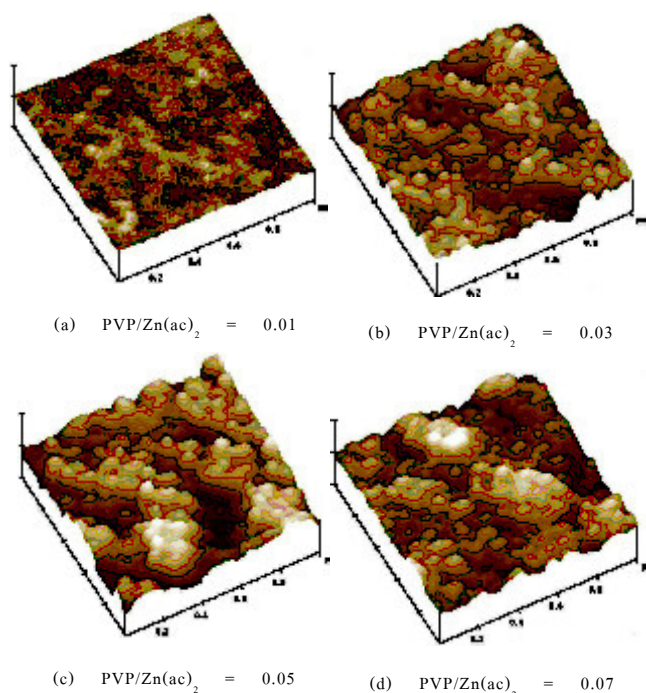
$$D = (0.9\lambda)/(\beta\cos\theta) \quad (1)$$

where D is the diameter of the crystallites forming the film, λ is the wavelength of $\text{CuK}\alpha$ line (0.15406 nm), β is full-width at half maximum (FWHM) in radian and θ is Bragg angle. The crystallite size of PVP-capped ZnO thin films gave a value in the same range of about 15-18 nm. However, the obtained crystallite size might deviate from the real value if the peak intensity is very low and the peak width is very large. Figure 1 also shows the growing film along the c-axis perpendicular to the substrate due to the adsorption of protonated PVP molecules on (100) negative planes, therefore; the grains grown in $\langle 001 \rangle$ direction and the more PVP concentration gave rise to higher (002) orientation (Casswell *et al.*, 2003). Moreover, the grains grew along the (002) plane because this plane occupied the lowest surface energy (Khranovskyy *et al.*, 2006). The other information on ZnO film characteristics derived by dip-coating on glass substrate from other researches are shown in Table 1.

Figure 2 shows the three dimensional AFM images taken at a scan area of $1.0 \times 1.0 \text{ nm}^2$. The AFM image shows that deposited films are crystalline and consist of grains with an average grain size of 48 nm at the mole ratio of PVP/ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ at 0.01 and an average grain size of 70

Table 1. The ZnO film characteristic derived by dip-coating on glass substrate from other researches.

| Researchers | Precursors | Solvents | Stabilizers (nm) | Grain size | Orientation | Annealing temperature (°C) |
|--|---|----------|---------------------------------------|------------|-------------|----------------------------|
| Murali K.R. (Murali <i>et al.</i> , 2007) | ZnCl ₂ | water | Acrylamide, Bisacrylamide | 50-150 | c-axis | 400-500 |
| Du T. (Du <i>et al.</i> , 2007) | Zn(CH ₃ COO) ₂ ·2H ₂ O | ethanol | PVP | 15 | - | 200 |
| Liu Z. (Liu <i>et al.</i> , 2007) | Zn(CH ₃ COO) ₂ ·2H ₂ O | ethanol | Polyethylene glycol diethanolamine | 200-400 | - | 500 |
| Ghansari M.S. (Ghansari <i>et al.</i> , 2007) | Zn(CH ₃ COO) ₂ ·2H ₂ O | ethanol | triethanolamine | 4-20 | random | 500 |
| Musat V. (Musat <i>et al.</i> , 2007) | Zn(CH ₃ COO) ₂ ·2H ₂ O | ethanol | monoethanolamine | 15-30 | - | 500 |

**Figure 2. AFM images of ZnO thin films at different mole ratios of PVP/Zn(CH₃COO)₂·2H₂O.**

nm at higher mole ratio of PVP/Zn(CH₃COO)₂·2H₂O. The surface roughness was determined using root mean square (RMS) roughness (ChangChun *et al.*, 2007).

$$RMS = \sqrt{\sum_{i=1}^N (z_i - z_a)^2 / (N - 1)} \quad (2)$$

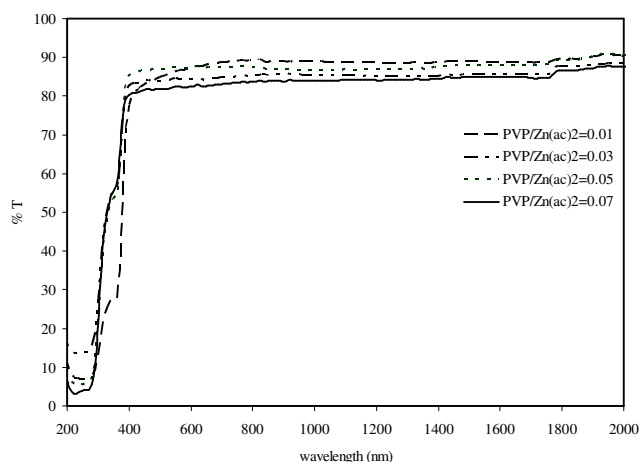
where z_i is the image height at pixel i , z_a is the average height and N is the number of pixels in the AFM image. The RMS roughness of thin films is 2.425, 7.209, 7.126, and 7.013 at the mole ratio PVP/Zn(CH₃COO)₂·2H₂O of 0.01, 0.03, 0.05 and 0.07, respectively. The surface roughness increased as a function of grain size, i.e. the higher surface roughness, the larger grain size. In this study, it was obvious that the RMS of ZnO thin films prepared at the mole ratio PVP/Zn(CH₃COO)₂ of 0.03, 0.05 and 0.07 was in the same range because these films gave the same average grain size.

3.2 Optical properties

In order to investigate the optical properties of thin films at various ratios of PVP/Zn(CH₃COO)₂·2H₂O, the transmittance was measured as a function of wavelength in the range of 200-2000 nm as shown in Figure 3. All the films showed the transmittance higher than 80% in the visible region. The optical absorption coefficient (α) was calculated from equation: $\alpha = (1/t)\ln[(1-R)/T]$ where t is thickness of thin film, T is transmittance and R is reflectance (Maity *et al.*, 2006). The fundamental absorption, which corresponds to the transition from valence band to conduction band, can be used to determine the optical band gap (E_g) by the equation below:

$$\alpha = A(h\nu - E_g)^n/h\nu \quad (3)$$

where $n = 0.5$ for direct transition, $n = 2$ for indirect transition, A is constant, h is Planck's constant (6.62×10^{-34} J.s) and n is frequency of incident photon. The ZnO material is direct transition and the plots of $(\alpha h\nu)^2$ vs. E (or $h\nu$) at various ratios of PVP/Zn(CH₃COO)₂·2H₂O are expressed in Figure 4. According to the dependence of the thickness,

**Figure 3. The optical transmittance spectra of ZnO thin films at different mole ratios of PVP/Zn(CH₃COO)₂·2H₂O.**

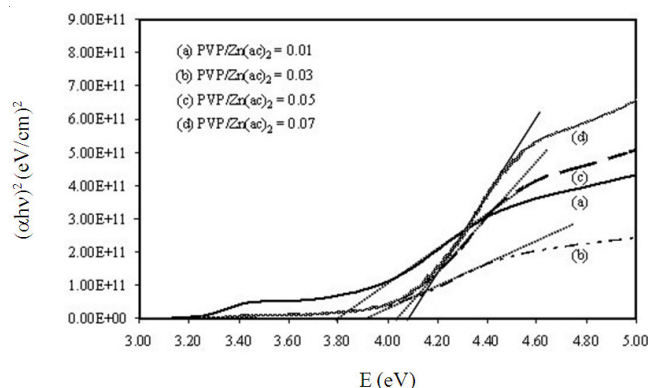


Figure 4. The evolution of the $(\alpha hv)^2$ vs. E (or $h\nu$) curves of ZnO thin films at different mole ratios of PVP/ $Zn(CH_3COO)_2 \cdot 2H_2O$.

therefore; the film thickness was controlled at about 600 nm in order to compare the band gap energy of all films in this study. The values of direct band gap (E_g) were obtained from the linear portion of the curve by extrapolation to zero of $(\alpha hv)^2$ at E-intercept. The ZnO thin films gave the optical band gap of 3.80, 3.90, 4.04 and 4.08 eV when using PVP of 0.08, 0.24, 0.40 and 0.56g, respectively (the mole ratio of PVP/ $Zn(CH_3COO)_2 \cdot 2H_2O$ = 0.01, 0.03, 0.05, and 0.07). These values are larger than the optical band gap of bulk ZnO material (3.37 eV) and also larger than the band gap of ZnO thin films (3.35 eV) which were encapsulated by PVP in the study of Tang *et al.*, (2006). The larger optical band gap of ZnO thin film in this study was due to the high crystalline quality (Chen *et al.*, 2007) and the lattice-match to the substrate (Abe *et al.*, 2007).

4. Conclusion

The ZnO thin films were successfully prepared by sol-gel dip-coating method. All films were dipped five times and calcined at 550°C in air for 1 hour. ZnO thin films exhibited preferred orientation along (002) plane when increasing PVP concentration into solution and these films gave the grain size of about 48 nm at PVP/ $Zn(CH_3COO)_2 \cdot 2H_2O$ = 0.01 and 70 nm at PVP/ $Zn(CH_3COO)_2 \cdot 2H_2O$ = 0.03, 0.05, and 0.07. Moreover, these ZnO thin films produced a large optical band gap of 3.80, 3.90, 4.04 and 4.08 eV at PVP/ $Zn(CH_3COO)_2 \cdot 2H_2O$ = 0.01, 0.03, 0.05, and 0.07, respectively. This large band gap may be due to the high crystalline quality and lattice-match to the substrate.

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