

SOL-GEL DEPOSITION OF ZnO:Al THIN FILMS

Phung Quoc Bao, Khuc Quang Dat and Nguyen Trong Nghia

College of Science, VNU

Abstract. Singlelayer aluminium-doped zinc oxide films were prepared on silicium substrates by the sol-gel spin coating process. The as-deposited films have been characterized by X-ray diffraction (XRD) and optical spectroscopy. All samples were polycrystalline with the hexagonal structure and the preferred [002] texture. Highly c-axis oriented ZnO:Al thin films were obtained by annealing at 520°C. The films exhibit an average UV-Vis transmittance of 87%. The two 325nm-excited PL bands were also observed at room temperature.

1. Introduction

Zinc oxide films and their doped forms are being extensively studied and widely used in various fields due to their high visible transmittance and low DC resistivity. These materials have great potential for applications in solar cells [1,2] and flat panel display electrodes [3]. A variety of deposition techniques has been utilized for fabricating doped and undoped ZnO thin films, such as pulsed laser ablation [4], sputtering [5,6], evaporating [7], spray pyrolysis [8] and sol-gel process [9,10].

Earlier, we reported the preparation of ZnO thin films by the sol-gel spin coating process from zinc acetate in ethylene glycol solution. Compared to ZnO films, Al-doped ones have lower resistivity and better stability. Furthermore, ZnO:Al films show comparable electrical and optical properties with those of Sn-doped In₂O₃ films (ITO) - the predominant transparent conductive oxide films [11].

In this paper, the structural, optical properties of ZnO:Al thin films prepared by the above-mentioned technique from zinc acetate dihydrate and aluminium nitrate in ethylene glycol solution have been investigated together with the effects of post-deposition treatment in air.

2. Experimental details

Preparation of films

Zn(CH₃COO)₂·2H₂O was first dissolved in an ethylene glycol solution at room temperature. The resultant solution was stirred at ca. 105°C in a condenser - fitted flask for 1 hour to yield a clear and homogeneous solution. Al(NO₃)₃·9H₂O was added and the similar procedure was carried out. The Al:Zn atoms ratio in consideration in this paper was 0.1 at% optimally obtained from experimental data. This sol solution was kept hermetically for 1 - 2 days before coating. Silicium slides

were cleaned by appropriate solvents. The coating solution was prepared by adding several drops of triethylamine to 3 ml of the sol solution, shaking and ultrasonication.

Thin films of ZnO:Al were prepared by the spin coating technique. The deposition solution was dropped on the glass substrate and spun at 2500 rpm for 30s. After coating, the precursor films were kept in humid air for 15 hours to facilitate hydrolysis. The films were then slowly heated to the desired high temperature and annealed for 3 hours to desorb solvents from the sample and to transform the adsorbed zinc complex into zinc oxide. The as-prepared films were highly transparent without any cracks. Fig. 1 shows the flow chart of the preparation of the ZnO:Al films.

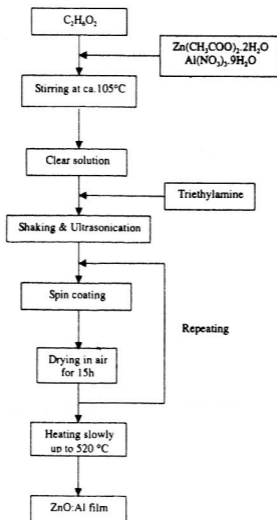


Fig. 1. Flow chart of the ZnO:Al film coating steps

Characterization of films

The structural properties of the obtained films were analysed by a Bruker Siemens D5005 X-ray diffractometer using $\text{CuK}\alpha$ radiation. 2θ - scans from 20° to 65° were performed at grazing incidence ($\theta = 2^\circ$). The crystallite size was calculated from the FWHM of the (002) peak corrected for the instrumental linewidth broadening using the Sherrer formula. Optical transmittance and UV-Vis-near IR absorption spectra were measured using a Shimadzu UV3101 double-beam spectrophotometer. Photoluminescence spectra were recorded by a Jobin Yvon F3-22 fluorometer.

3. Results and discussion

Structure properties

X-ray diffraction (XRD) was employed to determine the crystal structure of the as-deposited films. After the deposition, the films were dried in air. That made some weakly adsorbed compounds desorb from the films. Fig. 2a shows the XRD pattern of such a film. The ethylene glycol was totally desorbed without affecting the zinc complex. Zinc acetate dihydrate in ethylene glycol was transformed into zinc monoacetate $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)$ adsorbing on the substrate. The films crystallized in a monoclinic crystal structure with a strong orientation in (100) direction, corresponding to zinc monoacetate.

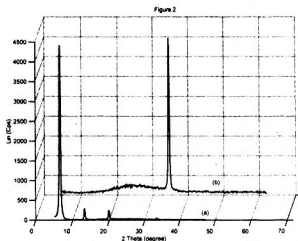


Fig. 2. XRD patterns of the as-deposited ZnO:Al films:

a) dried in air for 15h;

b) post-annealed in air at 520°C for 3h.

After annealing at 400°C, the (100) reflection of the monoclinic structure disappeared, the zincite hexagonal structure of ZnO was formed. By increasing the annealing temperature, the preferential orientation of the crystallites were more and more announced. Finally, at 520°C, the only very sharp (002) peak was observed in the XRD pattern (Fig. 2b). The highly c-axis oriented crystallites were then produced.

The (002) peak location was at $2\theta = 34.48^\circ$, very close to that of the standard ZnO crystal (34.45°). This implies that aluminium replaces zinc substitutionally in the hexagonal lattice.

As shown in Fig. 2, with increasing post-deposition heat treatment temperature, the locations of the recorded diffraction peaks do not change significantly, while their intensities become more intense confirming the improved crystallinity and the larger average grain size.

Optical properties

The aluminium-doped ZnO thin films were optically characterized through transmittance measurements in the near UV-Vis. Fig. 3 shows the optical transmittance spectrum for a typical sample of sol-gel synthesized ZnO:Al thin films annealed in air at 520°C. The average transmission over the 400-800 nm range is about 87%. There is a sharp increase intensity of transmitted light around 380 nm due to band edge absorption. The band-gap of ZnO:Al calculated from the straight part of the optical transmittance spectrum is close to the intrinsic band-gap of ZnO (3.2 eV).

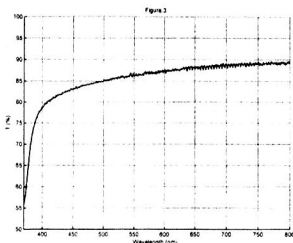


Fig. 3. UV-Vis transmittance spectrum of the ZnO:Al films post-annealed in air at 520°C for 3h.

Fig. 4 displays a typical photoluminescence (PL) spectrum of the so-obtained ZnO:Al thin films excited by 325 nm radiation. No significant difference from that of ZnO thin films prepared by the same deposition procedure was observed. The PL spectrum consists of the excitonic band centered at ca. 380 nm and the characteristic green emission at ca. 500 nm. That holds for the Al / Zn ratios under consideration.

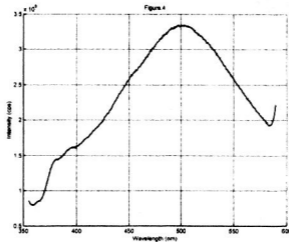


Fig. 4. Photoluminescence spectra of the ZnO:Al films post-annealed in air at 520°C for 3h.

4. Conclusion

We have presented the preparation of ZnO:Al thin films on silicon substrates by sol-gel spin coating process with zinc acetate dihydrate and aluminium nitrate as precursors. Triethylamine was used as gel stabilizer. The as-deposited thin films were slowly postheated up to different temperature values, once dried in air for 15 hours. The X-ray diffractometer measurements revealed that all samples were polycrystalline with the hexagonal structure and the preferred (002) texture. The highly c-axis oriented ZnO:Al thin films were obtained by postheating at 520°C. The XRD analysis is in accordance with the TGA/DTA investigation reported elsewhere [12]. The typical transmittance spectrum near UV-Vis displays an absorption edge at ca. 370 nm and an average transmittance of 87%. While excited by 325 nm radiation, the films exhibit the two PL bands similar to those of undoped sol-gel derived ZnO thin films [13]. Sol-gel derived Al-doped ZnO thin films do not show any considerable changes in both structural and optical properties characterizing undoped ZnO thin films with the Al:Zn ratios under

study. The as-deposited ZnO:Al thin films have globally better DC conduction than similarly processed ZnO ones. Their electrical properties are thoroughly investigated and will be subject to further publication. *

References

1. M. Bouderbala et al., *Applied Energy* **64**(1999) 89-96.
2. D. G. Baik, S. M. Cho, *Thin Solid films*, **354**(1999) 227-231.
3. M. Chen et al., *Materials Science and Engineering*, **B85**(2001) 212-217.
4. K. L. Narasimhan et al., *Thin Solid films*, **295**(1997) 104-106.
5. M. Chen et al., *Materials Letters*, **48**(2001) 194-198.
6. D. H. Zhang et al., *Materials Chemistry and Physics*, **68**(2001) 233-238.
7. M. Jin et al., *Thin Solid Films*, **357**(1999) 98-101.
8. K. H. Yoon, J. Y. Cho, *Materials Research Bulletin*, **35**(2000) 39-46
9. D. Bao, H. Gu, A. Kuang, *Thin Solid Films*, **312**(1998) 37-39.
10. T. Schuler, M. A. Aegerter, *Thin Solid Films*, **312**(1998) 37-39.
11. M. Tzolov et al., *Thin Solid Films*, **351**(1999) 125-131.
12. R. F. Silva et al., *J. of Non-Crystalline Solides*, **247**(1999) pp. 243-253.
13. Khuc Quang Dat et al., *Proc. of the 3rd Nat. Conf. on Solid-State Phys., Nhatrang*, August 8 -10, 2001.