

Preparation and Characterisation of ZnO Thin Films by Spray Pyrolysis Method

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Abstract

Zinc oxide (ZnO) thin film is a transparent conducting oxide thin film and has attracted significant attention because of its potential applications in optoelectronic, solar cells and heat mirrors. The ZnO thin films were deposited by spray pyrolysis method. The films were grown on glass substrates at 415, 445, 475 and 505 °C substrate temperatures.

The transmittance in the visible region and energy band gap values range from 79% to 85% and 3.32 to 3.34eV respectively. Raman spectroscopic analysis indicates that there are two peaks at 436 and 556 cm^{-1} . It was concluded that ZnO thin films with optimal growth conditions using spray pyrolysis is an excellent material for transparent conducting oxide films.

Keywords; Thin film, Spray pyrolysis, Optoelectronic, Transparent, Conducting, Oxide

Introduction

Transparent conducting oxide (TCO) films have attracted significant attention, because of their potential applications (1). They are also highly degenerative and usually have low resistance (2). The application of transparent conducting oxide materials in various fields such as solar cells, heat mirrors and gas sensors have caused a great increase in research on these materials (5).

Among transparent conducting oxide materials, Zinc Oxide has unique advantages over other materials due to its higher thermal stability in hydrogen plasma atmosphere, low price and its non-toxicity. These interesting properties prove that it is one of the promising materials in the number of electronics, optoelectronics, and sensors applications (3)

The increasing use of transparent conducting electrode for many optical devices like flat panel displays, heat mirrors, solar cells etc. have stimulated more researches to develop inexpensive materials. ZnO is a promising material for light-emitting devices of short wavelength from blue to ultraviolet (UV). Also, it shows great potential for application in the development of optoelectronic devices (6). The conductivity of ZnO thin films depends upon several factors, such as the preparation technique, the preparation parameters, the doping agent, and the annealing conditions. Because of their chemical stability, the ZnO films are more useful in the fabrication of thin-film solar cells, compared to Sn-doped In_2O_3 (ITO). ZnO films appear to be the best choice for the contact and window layer in CdTe, CuInSe_2 and $\text{Cu}_2\text{ZnSnS}_4$ based solar cells, which are among the leading contenders for practically large-scale photovoltaic systems (4). For different applications such as a Si:H based solar cells and flat panel displays, good-quality ZnO-based materials would have several advantages over

the more conventional Indium Tin Oxide (ITO) layers, including lower cost of raw material, stability during reduction by hydrogen in processing plasmas, low toxicity, and better patterning characteristics (9).

Experimental Procedure

The glass slides used as substrates were first cleaned with water and detergent, then ultrasonically cleaned for ten minutes with isopropyl alcohol using a Bandelin Sonorex RK 100 ultrasonic cleaner, then cleaned with deionised water and blown to dry with N₂ gas before they were introduced into the stage of the spray pyrolysis system. In the work the ZnO film was prepared using the spray pyrolysis method at 415, 445, 475 and 505 °C substrate temperatures. 0.2 M solution of zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] diluted in methanol and deionized water (3:1) was used for the film. A few drops of acetic acid were added to improve the clarity of solution. Nitrogen was used as the carrier gas, with pressure at 0.2 bar. The ultrasonic nozzle to substrate distance was set at 30cm and during the deposition, the solution flow rate was held constant at 4 ml/min. The deposition time was about 5 min. The film samples were subjected to evaporation temperature of 160 °C for twenty minutes. After the deposition, the samples were annealed at 300°C for one hour. The optical transmittance of the films was measured with an ultraviolet-visible-near infrared spectrophotometer, the thickness of the films was measured using a profilometer and the band gap energy was calculated from the thickness and transmittance values. Finally the Raman peaks were determined using the Raman spectroscopy.

Results and Discussion

Optical Transmittance

The results of the optical transmittance for the different samples studied revealed that the optical transmittance values range from 79% to 85%. The values of the transmittance for all the samples were high as seen and the transmittance curves as a function of wavelengths from 250nm to 800nm are shown in fig 1.0. Optical properties of ZnO:Al thin films include transmittance in the visible region and a high optical transmittance is one of the most important parameters required for its application in solar cell windows and optoelectronic devices.

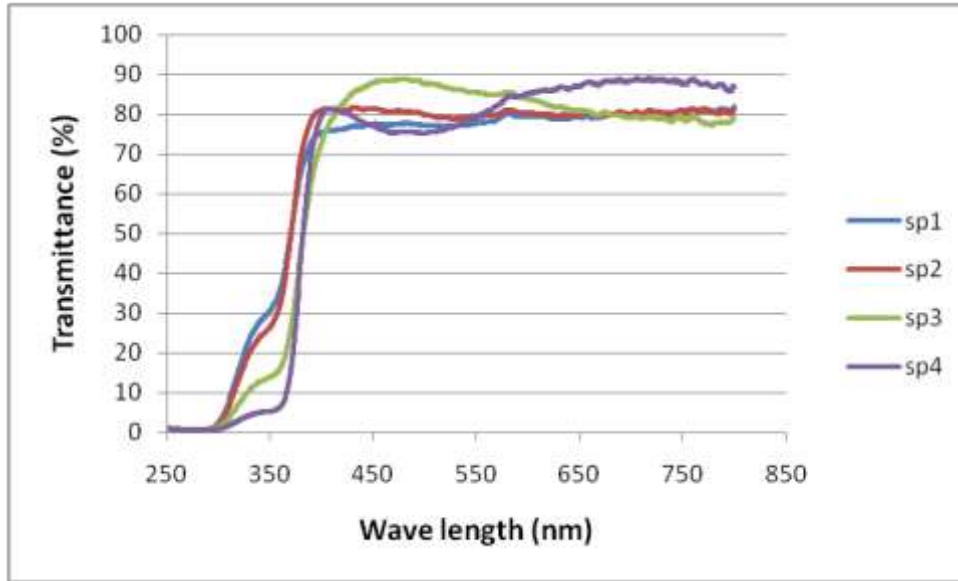


Fig. 1.0; optical transmittance spectrum for samples sp1-sp4

Note that sp1, sp2, sp3, and sp4 are sample deposited at 415, 445, 475 and 505 °C

Energy Band Gap

The band gap energies were obtained from the UV spectroscopic measurements. It is well known that the optical absorption determines the optical band gap and ZnO thin films have a direct band gap. The optical band gap E_g for direct band gap semiconductor is given by

$$\alpha h\nu = C(\hbar\nu - E_g)^{1/2} \tag{2}$$

Where $h\nu$ is the photon energy, C is a constant for a direct transition, and α is the optical absorption coefficient and it is determined by

$$\alpha = (1/d)\ln(1/T) \tag{3}$$

Where d is the film thickness and T is the optical transmittance. Figures 2.0 shows curves for $(\alpha h\nu)^2$ as a function of $h\nu$ for obtaining the optical band gap, which was derived from transmittance spectrum. The energy gap was obtained by extrapolating the linear absorption edge part of the curve to the intersection with energy axis. The band gap values obtained from the curves were 3.32eV, 3.33eV, 3.29eV and 3.34eV for samples sp1, sp2, sp3 and sp4 respectively. These values are in agreement with those obtained by Ali *et al.*, (2006) and Pei *et al.*, (2006)

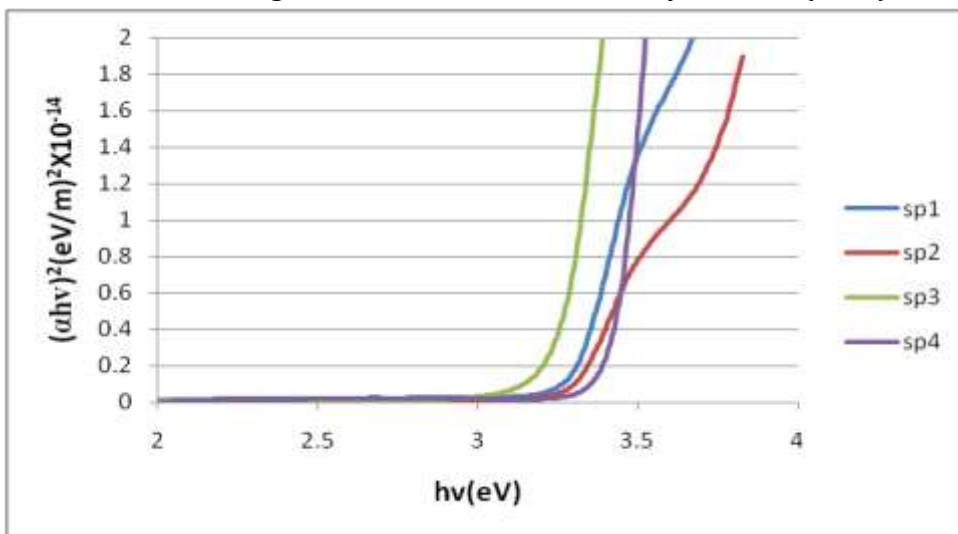


Fig. 2.0; Measurement of band gap energy for sp1-sp4

Note that sp1, sp2, sp3, and sp4 are sample deposited at 415, 445, 475 and 505 °

Raman spectroscopy is a means to distinguishing possible secondary phases present in ZnO thin film samples. It has to be noted, however, that with the typical laser excitation sources (~ 300 to 650 nm) used in Raman spectroscopy, the light penetration depth is in the order of hundred nanometers or less (the penetration depth can be roughly estimated as $1/(2\alpha)$, where α is the sample absorption coefficient) and therefore only the surface region of the samples can be explored in planar configuration. In-depth analysis can be performed using the sample cross-section, or by measuring the Raman spectra while sputtering the sample to different depths.

The clear Raman spectra of the ZnO thin films samples showing the characteristic peaks at 436 and 556 indicating pure phases is shown in Fig. 3.0 below.

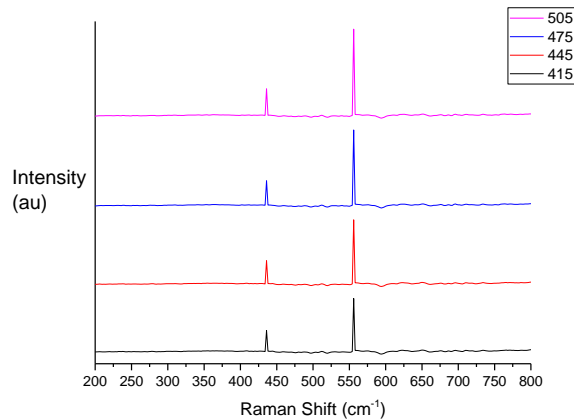


Fig. 3.0 Raman Spectra for substrate temperatures 415 to 505

CONCLUSION

In summary, transparent conductive ZnO thin films have been deposited on glass substrates by spray pyrolysis method at 415, 445, 475 and 505 substrate temperatures. The transmittance spectrum shows that there are significant changes for ZnO films deposited at different temperatures. The transmittance in the visible region and the energy band gap values range from 79% to 85% and 3.32 to 3.34eV respectively which is a confirmation of its potential for use in solar cell windows and other optoelectronic applications. Raman spectra exhibited peaks at 436 and 556 cm^{-1} which indicates that the films are of pure phase.

It can be concluded that ZnO thin films with optimal growth condition when using spray pyrolysis can be an excellent materials for transparent conducting film, including solar-cell electrodes.

RECOMMENDATIONS

It is recommended that furthered research should consider using more variety of deposition parameters and doping to improve material quality.

It is also recommended that a comparative study of different elemental doping compositions such as $\text{SnO}_2:\text{F}$, $\text{In}_2\text{O}_3:\text{Sn}$ etc should be grown to determine the desirable properties of the films and also to be able to determine which film has more desirable parameters than the other.

Any further research on this topic should also include structural characterization using scanning electron microscope (SEM) and X-ray diffractometer (XRD) so as to be able to determine the grain size, surface morphology and axis orientation of the deposited thin films.

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