Growth and Characterization of ZnO Nano thin films using Spray pyrolysis

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Abstract

This paper presents the deposition of polycrystalline ZnO thin films on glass substrate by spray pyrolysis technique at 250°C using aqueous solution of zinc acetate. The characterization studies were performed. From the transmission spectrum within the region of UV-VIS-NIR, the optical constant such as refractive index and extinction coefficient were determined. The films were found to exhibit a low absorbance and reflectance and high transmittance in the visible region. The thickness and band energy gap of thin films were evaluated as 1.9 µm and 3.2 eV respectively. The atomic force microscopy (AFM) image is used to analyze the morphological structure of ZnO film. The X-Ray diffraction study reveals that the developed films were polycrystalline with preferred orientation and are ⊥ to the substrate surface and grain size is to be 0.43nm.

Keywords: ZnO, Thin film, Spray pyrolysis technique, optical properties, X-ray diffraction.

Introduction

ZnO is an II – VI compound of n-type semiconductor has a direct band gap of about 3.3eV with an hexagonal wurtzite structure, similar to GaN and ZnSe[1]. Compare with other materials such as In2O3, Cd2SnO3 or SnO2, ZnO has some advantages due to its unique combination of attractive properties like non toxicity, optical, good electrical and piezoelectric behavior and its low cost. Due to these properties, ZnO is a promising material for electronic or optoelectronic applications such as solar cells (antireflection coating and transparent conducting materials), gas sensors, liquid crystal displays, heat mirrors, surface acoustic devices etc.. In addition to that it could be also used in integrated optics [2].

Different techniques such as chemical vapour deposition, plasma arc enhanced chemical vapour deposition, solgel, reactive evaporation, rf magnetron sputtering, spray pyrolysis, molecular beam epitaxy, pulsed laser deposition etc. have been used for the deposition of ZnO thin films and each methods has its advantages and limitations. Among various techniques spray pyrolysis deposition (SPD) techniques provides a simple route of synthesizing thin films because of its simplicity and low cost and also it is used for coating large area thin film deposition without any high vacuum system[3,4].

For some of the applications like gas sensor & solar cells, it is necessary to perform an accurate characterization of optical properties which include refractive index and optical losses. Many more works has been done on these materials but still new approach is coming up to find simple route and to synthesis quality films for better performance.

In view of the importance of these materials in the field of optoelectronic devices particularly solar cells , we have synthesized high purity ZnO films for 50 ml solution at relatively low temp(250°C) by using SPD system , so as to reduce the preparation cost[5].Hence in this paper we report results of optical characteristics and XRD.

Experimental details

The deposition of ZnO thin film in the present work was carried out by SPD technique. Fig.1 shows the schematic diagram of the spray pyrolysis setup. The deposition setup includes the precursor solution, carrier gas assembly connected to spray nozzle.

We prepare 0.05M aqueous solution of Zinc acetate (Zn(CH3COO)2 . 2H2O) as the precursor of the film. The solution was sprayed on pre-cleaned commercial glass substrate which was ultrasonically cleaned by deionized water and acetone before coating. The substrate temperature was maintained at 250°C ± 5°C during deposition. The diameter of the spray nozzle is 0.03mm and distance between substrate and spray nozzle was fixed at 25cm. The solution spray rate was maintained...
at 3ml per minute throughout the spray process. The pressure of carrier air gas was kept constant at 1 bar.

The possible chemical reaction takes place on the heated substrate to produce ZnO thin film maybe as follows. When the droplet of solution reach the heated substrate, chemical reaction of the Zinc Acetate with water solution takes place under stimulated temperature and provides the formation of ZnO thin films[2].

\[
\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O} \xrightarrow{250 \degree \text{C}, \text{deposited as}} \text{ZnO}+\text{CO}_2+\text{CH}_4+ \text{steam}
\]

The X- ray Diffractometer with CuKa radiation with \( \lambda = 1.5405 \text{ Å} \) (30Kv, 15mA, scanning speed=2°/min) was used to investigate the crystallographic structure of thin film. The optical transmission of ZnO films were carried out with a double beam Spectrophotometer in the UV-VIS-NIR region. The optical transmittance at normal incidence was recorded in the wavelength range 300 – 700 nm[6,7].

**Results and Discussion**

XRD pattern of ZnO thin films deposited at 250 \degree C present with only one sharp peak was obtained with 2\( \Theta \) from 10 to 60 \degree C at a glancing angle of 6\( ^\circ \) is crystallized in Wurtizite phase with a preferential orientation along c axis is shown in fig 2. The strongest peak observed can be attributed to (002) hexagonal plane. The grain size can be estimated using the Scherrer’s relation [8].

![Fig 2. Xray diffraction pattern of ZnO thin film deposited on glass substrate at 250\degree C.](image)

\[
g = \frac{0.94 \lambda}{\beta \cos \Theta}
\]

Where \( \lambda \) is the wavelength of X-ray i.e 1.5405\( \text{Å} \), \( \beta \) and \( \Theta \) are the full width half maximum and angle of Braggs diffraction of the 002 diffraction peak respectively and the crystalline size was estimated about 0.43nm.

The thickness of the film was calculated using the gravimetric weight difference method and was found to be 1.9 \( \mu \text{m} \) with the relation \( t = \frac{m}{(\rho \times A)} \) where \( m \) is the mass of the deposited film on the glass substrate, \( A \) is the area of the deposited film and \( \rho \) is the density of the deposited material(ZnO = 5.61 g/cm\(^3\)) [9,10].

Transmission and absorbance spectra of ZnO thin films are present in Fig 3 & 4. It shows very low absorbance and high transmittance (about 80%) in the visible region. The optical constant such as refractive index (n) and extinction coefficient (k) were determined from the transmittance spectrum. The variations of refractive index (n) and extinction coefficient (k) with wavelength in the region of 400 nm – 700 nm are shown in fig 5 & 6. The absorption coefficients alpha of ZnO thin films was determined from the measurements of transmittance. If the thickness (t) of the film is known the absorption coefficient (\( \alpha \)) can be determined from the following relations [11-13].

![Fig 3. Optical transmission curve of ZnO thin film.](image)

![Fig 4. Optical absorbance curve of ZnO thin film.](image)

![Fig 5. Plot of wavelength versus refractive index.](image)

![Fig 6. Plot of wavelength versus extinction coefficient.](image)
The energy gap was determined by using the absorption coefficient values. Fig. 7 shows the plot of \((\alpha h\nu)^2\) versus hv, where \(\alpha\) is the optical absorption coefficients and hv is the incident photon energy[14]. By assuming a direct transmission between valence band and conduction band the energy gap was estimated.

\[
\alpha = \frac{\ln(T)}{t}
\]

Where K is a constant extrapolating the straight line on the curve, so that \(\alpha h\nu = 0\). From this the energy gap \(E_g = 3.2\) eV is determined.

AFM measurement performed to study the surface morphology of the ZnO thin film. Fig. 8 shows the 2D AFM images. Micrographs reveal that films are closely packed and granular in nature; signature of agglomeration of grains is almost absent. AFM images have also been utilized to estimate the grain size of the samples. Uniform brightness contrast exhibits absence of impurities or clusters[15,16].

**Conclusion**

The present work reports successful preparation and characterization of highly transparent Zinc oxide thin films at 250°C using spray pyrolysis technique. The characterization studies include X-ray diffraction (XRD), optical studies and Atomic Force Microscopy (AFM). The result of XRD clearly reveals polycrystalline nature of ZnO films with hexagonal wurtzite structure and \(0 0 2\) preferential orientation. The grain size was computed to be 0.43nm. The films exhibit excellent optical properties with transmittance (about 80%), low absorbance and reflectance in the visible region. The data extracted from transmittance, reflectance and absorbance spectra were used to determine various optical constants such as refractive index, extinction co-efficient and energy Band gap. The developed films have a direct band gap value of 3.2 eV which is close to the reported value 3.37 eV from the literature. The characterization studies confirm the suitability of deposited ZnO thin films for using them in optoelectronic devices and solar cells.

**Reference**


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