

Role of ZnO as a Transparent Layer in Thin Film Solar Cells Using Spray Pyrolysis Technique

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Abstract

A versatile and cost effective spray pyrolysis technique was used to prepare the Zinc Oxide (ZnO) thin film on a glass substrate. The feature of the obtained film was characterized using Glancing incidence angle X-ray diffraction (GIXRD), Scanning Electron Microscope (SEM), UV-Visible Spectroscopy and Photoluminescence (PL). GIXRD confirmed that the structure of the ZnO film was polycrystalline having wurtzite structure. SEM image revealed root-like morphology on the surface of ZnO thin film and the shortest root diameter was about 91.2 nm. From UV-Visible spectrum an optical transmittance of about 85% in the visible region and direct optical band gap energy of 3.2 eV was calculated. The PL analysis showed that the film exhibited a strong emission peaks at violet and green region. From the characterized results, spray pyrolysis is the viable technique to deposit ZnO thin film on a glass substrate, which can be used as a transparent layer in thin film solar cells.

Keywords: ZnO Thin Film, Spray Pyrolysis, Transparent layer, Solar Cell.

1. Introduction

Recently, Zinc oxide film has gained more attention due to its potential use in many applications such as transparent conductive electrode, solar cell, gas sensor, light emitting

diodes, lasers and varistors which attributed to its wide and direct band gap (3.37 eV) and a larger exciton binding energy (60 meV) [1]. In particular, ZnO is nontoxic and also provides good transparency, high electron mobility, chemical and thermal stability which perfectly matches the requirement of transparent contacts in photovoltaic cells [2]. ZnO thin films have been deposited by different deposition techniques like chemical vapour deposition (CVD) [3], magnetron sputtering [4], pulsed laser deposition (PLD) [5], electron beam evaporation (EBM) [6]. Most of these methods need high vacuum and high operating temperatures to work, which make them high cost techniques. Chemical based solution routes such as sol-gel [7], co-precipitation [8] and spray pyrolysis [9] can be considered as simple and economic methods involving low cost equipment and raw materials.

Among these chemical based techniques, spray pyrolysis is a useful alternative to the traditional methods for obtaining pure ZnO thin films. It is of particular interest because of simplicity, low cost of the source materials, producing high quality films and minimal waste production. The spray pyrolysis process allows the coating of large surface area and uniform deposition with very thin layers with specific composition, morphology, good adhesion between the deposited films [10].

In the present work, ZnO thin film is prepared using the spray pyrolysis technique and show high optical transmittance in UV, VIS and IR regions which is suitable material for transparent layer on solar cell. The structural, morphological, optical properties of the deposited ZnO thin film is studied using Glancing incidence angle X-ray diffraction (GIXRD), scanning electron microscope (SEM), UV-visible spectroscopy and fluorescence spectroscopy.

2. Experimental Procedure

Thin film of ZnO was deposited on a glass substrate by simple and economical spray pyrolysis technique. A solution of 0.1 M using zinc acetate dihydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ was used as a precursor prepared by dissolving in mixture of deionized water and isopropyl alcohol (2: 3) volume ratio. The film has been deposited on ultrasonically cleaned glass substrates kept at $450^\circ C$. The nozzle was at a distance of 20 cm from the substrate during deposition. The solution flow rate was held 4ml/min. Compressed air was used as a carrier gas. The pressure was maintained at 1.2 kg/cm². This results in the formation of well adherent and uniform ZnO film. The as deposited film of ZnO was transparent with light whitish color.

The crystal structure and phase identification of the prepared ZnO thin film was characterized using Glancing incidence X-ray diffractometer (XPRT PRO) at a scanning range of 20° to 80° with $CuK\alpha 1$ source radiation ($\lambda = 1.54051 \text{ \AA}$). The surface morphology of the thin film was examined using scanning electron microscope (SEM). The optical properties of the ZnO thin film were determined by UV-Visible spectrometer (Model-lambda) in the wavelength range of 300-1100 nm. The room temperature photoluminescence characteristic of

ZnO film was investigated using Perkin Elmer (Model- Lambda 45).

3. Results and Discussion

The crystallinity, crystallographic orientation and phase evaluation of the ZnO thin film prepared at $450^\circ C$ is studied by Glancing incidence x-ray diffraction (GIXRD) is shown in Fig. 1. The diffraction peaks obtained between the 2θ ranges are from $20^\circ - 80^\circ$. Seven diffraction peaks were observed at $2\theta = 31.9^\circ, 34.6^\circ, 36.5^\circ, 47.7^\circ, 56.9^\circ, 63.0^\circ, 69.5^\circ$ which can be attributed to (100), (002), (101), (102), (110), (103) and (112) planes of ZnO thin film obtained by IPA solution. The sharp and narrow diffraction of the peaks demonstrated that all ZnO thin film is of good crystalline in quality and also found that, the films are polycrystalline with hexagonal wurtzite structure. Here the film exhibits highest peak at (101) plane with preferential orientation which is located at $2\theta = 36.5^\circ$. This can be due to the highest density of Zn atoms in this plane. The other small peaks which are shown in figure are due to the non-decomposed organic compounds or impurities in the solution used for deposition of the film.

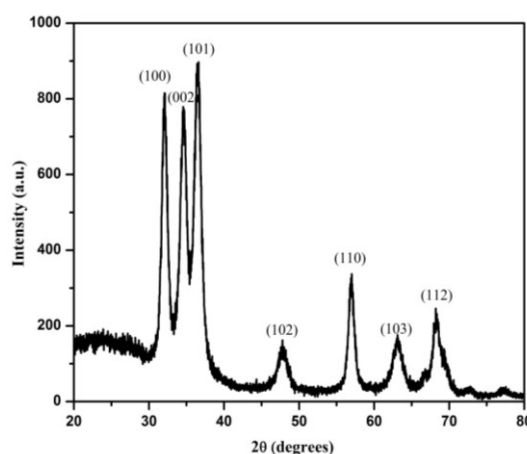


Figure 1. GIXRD pattern of ZnO thin film

The crystallite size of the deposited film is calculated using the Scherer's equation [11]

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is the crystallite size, λ is the wavelength of the target $\text{CuK}\alpha 1$ ($= 1.54051 \text{ \AA}$), β is the full-width half maximum value and θ is the position of respective Bragg peaks. The crystallite size of ZnO is calculated along this plane, which gives the value of 10 nm.

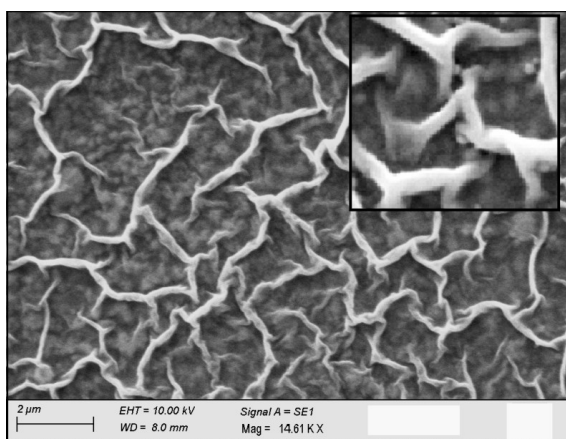


Figure 2. SEM image of ZnO thin film

The surface morphology and size of the zinc oxide thin film using scanning electron microscope technique is shown in Fig 2. SEM micrograph reveals that the ZnO film exhibit root-like structure. The texture of the film is found to be crack free and having uniform morphology over the entire film. In ZnO image, the particles are linked to each other to make long structure of ZnO which is called root-like morphology [12]. The average diameter of the shorter root-like is about 91.2 nm.

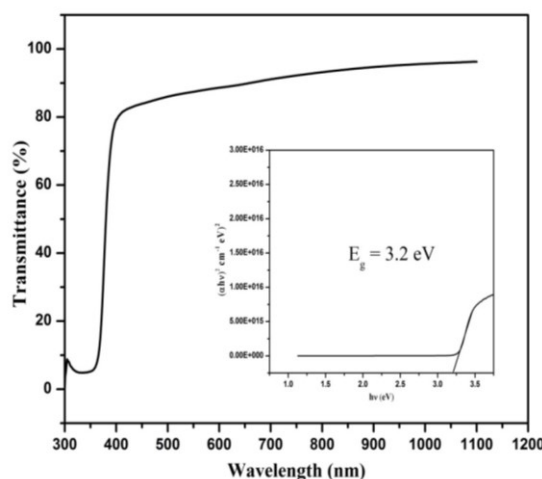


Figure 3.1. UV transmittance spectrum with tauc plot of ZnO thin film (inset shows the band gap energy of the material)

The optical transmission spectrum obtained in the wavelength range of 300 to 1200 for the deposited ZnO film is shown in the Fig 3.1. From UV-Visible spectrum it is clear that the film shows high transparency in the visible region with an average transmittance reaching up to 85%, which indicates the better crystal structure with less defects. A sharp ultraviolet cut-off at approximately 333 nm is observed for the prepared film. The high transparency obtained for the ZnO film in the visible region shows its potential application in the solar device applications.

The optical band gap energy is calculated using Tauc plot is shown as the inset in Fig 3.1. The direct band gap energy obtained from the extrapolation of the linear part of the curve in the plot of $h\nu$ in eV versus $(\alpha h\nu)^2$ in $(\text{cm}^{-1} \text{ eV})^2$. The absorption coefficient (α) of the deposited film is determined from the equation related to the photon energy is given by

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

where E_g is the energy band gap of the semiconductor, A is a constant, and $n = 1/2$ for direct

allowed transitions. The Tauc plot gives the direct band gap of the samples and calculated band gap is found to be 3.21 eV which is matching well with of the reported values.

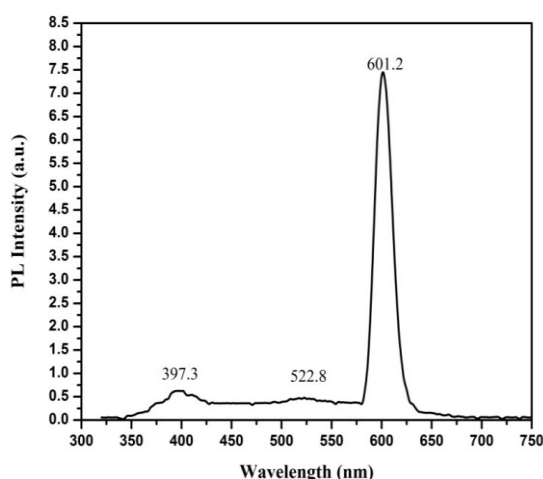


Figure 3.2. Photoluminescence spectrum of ZnO thin film

The luminescence property of deposited thin films is studied using photoluminescence spectroscopy. The photoluminescence (PL) spectrum of prepared ZnO thin film is depicted in fig 3.2. The spectrum of ZnO film showed that the near band edge (NBE) emission is in the UV region and the deep-level emission (DLE) in the visible spectrum composed of green and red bands [13]. A low intensity with broad emission peaks centered at 397.3 nm in the UV region is attributed to the recombination of free excitons in the surfaces of ZnO particles. And also another low intensity with broad peak located at 522.8 nm in the green emission region which is due to impurities and structural defects. A strong peak located at 601.2 nm, which is in red band emission that can be attributed to the presence of excess oxygen.

4. Conclusions

In this present work, the highly transparent ZnO thin film was prepared by spray pyrolysis technique. The GIXRD pattern showed that the deposited film had a polycrystalline hexagonal wurtzite structure with strong orientation along (101) plane with an average crystalline size was about 10 nm. The SEM image revealed that the ZnO film exhibited root-like morphology with uniform distribution. The investigation from UV-Visible spectrum showed that the obtained film was highly transparent in the visible region with an average transmittance reaching upto 85% with the better crystalline nature with less defects. PL spectrum of the film showed emission in both UV and visible region. The simple and low-cost spray pyrolysis technique offers an attractive alternative to the PVD or CVD fabricated ZnO films. The above mentioned results showed that the deposited ZnO film with good crystallinity and high transparency is a promising n-type material for thin film solar cell.

References

- [1] Godbole, B., Badera, N., Shrivastava, S., Jain, D. and Ganesan, V., "Growth Mechanism of ZnO Films Deposited by Spray Pyrolysis Technique", Mater. Sci. Appl., 2, 2011, pp. 643–648.
- [2] Vimalkumar, T.V., "Highly conductive and transparent ZnO thin film using Chemical Spray Pyrolysis technique: Effect of doping and deposition parameters", Cochin University of Science and Technology, Cochin, Kerala, Doctoral Thesis, 2011.
- [3] Purica, M., Budianu, E., Rusu, E., Danila, M., and Gavrilă, R., "Optical and structural investigation of ZnO thin films prepared by

- chemical vapor deposition (CVD)", *Thin Solid Films*, 402-403, 2015, pp. 485-488.
- [4] Dave, P.Y., Patel, K.H., Chauhan, K.V., Chawla, A.K. & Rawal, S.K., "Examination of Zinc Oxide Films Prepared by Magnetron Sputtering", *Procedia Technol.*, 23, 2016, pp.328-335.
- [5] Ramamoorthy, K., "Development of a novel high optical quality ZnO thin films by PLD for III-V opto electronic devices", *Curr. Appl. Phys.*, 6, 2006, pp. 103-108.
- [6] Giri, P. K., "Studies on zinc oxide nanorods grown by electron beam evaporation technique", *Synth. React. Inorganic, Met. Nano-Metal Chem.*, 37, 2007, pp. 437-441.
- [7] Anand, V.K., Sood, S.C. and Sharma, A., "Characterization of ZnO thin film deposited by sol-gel process", *AIP Conf. Proc.*, 1324, 2010, pp. 399-401.
- [8] Kolodziejczak-Radzimska, A. and Jesionowski, T., "Zinc oxide-from synthesis to application: A review", *Materials (Basel)*, 7, 2014, pp. 2833-2881.
- [9] C. Nehru, L., Umadevi, M., and Sanjeeviraja, C., "Studies on Structural, Optical and Electrical Properties of ZnO Thin Films Prepared by the Spray Pyrolysis Method", *Int. J. Mater. Eng.*, 2, 2012, pp. 12-17.
- [10] Tarwal, N. L., "Growth of multifunctional ZnO thin films by spray pyrolysis technique", *Sensors Actuators, A Physl.*, 199, 2013, pp. 67-73.
- [11] Mahmoud, F.A., and Kiriakidis, G., "Nanocrystalline ZnO Thin Film for Gas Sensor Application", *Bull. Mater. Sci.*, 5, 2009, pp. 15-20.
- [12] Komaraiah, D., "Optical, Structural and Morphological Properties of Photocatalytic ZnO Thin Films Deposited by Spray Pyrolysis Technique", *Mod. Res. Catal.*, 5, 2016, pp. 130-146.
- [13] Inguva, S., Vijayaraghavan, R.K., McGlynn, E., and Mosnier, J.P., "Highly transparent and reproducible nanocrystalline ZnO and AZO thin films grown by room temperature pulsed-laser deposition on flexible Zeonor plastic substrates", *Mater. Res. Express*, 2, 2015, pp.96401.