International Journal of Engineering & Scientific Research
Vol. 6 Issue 1, January 2018, (Special Issue ICON17-MCC)
ISSN: 2347-6532 Impact Factor: 6.660
Journal Homepage: http://www.esrjournal.com Email: esrjeditor@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Optical and electrical properties of multi-layer ZnO thin films and their photo-catalytic activity for water treatment

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Keywords:

Multi-layer ZnO
Structural properties
Optical properties
Electrical properties
Photo-catalytic activity

Abstract

Transparent zinc oxide (ZnO) thin films were prepared on glass substrates by the sol-gel spin coating method using zinc acetate dihydrate as the precursor material of ZnO. ZnO films were preheated at 100°C and again spin coated for making multi-layer films. The ZnO films were characterized with optical transmittance measurements using UV-Visible spectrophotometer. The optical band gap energy was estimated by Tauc method and found to be decreased with increase of number of layers of ZnO film. The electrical resistivity of ZnO thin films was measured by four probe meter after annealing the films at 400°C in air for 1h. The electrical resistivity decreased with increasing the number of layers of ZnO film. The photo-catalytic activity of ZnO film was studied under UV light for the purification of water by dissolving a poisonous dye in water. It has been observed that the concentration of the dye decreased with increasing the UV irradiation time and the number of layers of ZnO film.

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1.0Introduction

Zinc oxide (ZnO) thin films are highly transparent in the UV visible region and highly conducting. They are n-type semiconductors with wide and direct band gap of 3.37 eV and high exciton binding energy of 60 meV. They are highly (002) oriented and columnar grain structured so that they can be used in non-volatile memory applications [1]. ZnO thin films are widely used for various applications such as conducting electrodes in solar cells [2] , n-channel thin film transistors [3], gas sensors[4], biomedical sensors [5], optoelectronic devices [6] etc. ZnO thin films can be synthesized in various forms such as nanowires [7], nanorods [8], nanotubes [9], etc.

During the last one decade renewed interest has been denoted to ZnO based materials owing to their applications in the field of optoelectronic devices, semiconductor diode lasers and photoelectrochemical water splitting. ZnO thin films can be fabricated by many techniques like

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spray pyrolysis [10], sol-gel method [11], Rf magnetron sputtering [12], electron beam evaporation technique [13] etc. Basic properties of ZnO thin films can be fine tuned by many factors at the time of deposition.

In the present work we have prepared ZnO thin films by the sol-gel spin coating method. They are characterised for various properties like optical using UV visible spectrophotometer, electrical by four probe method and structural by x-ray diffraction (XRD). The electrical properties were calculated by using four point probe technique (KIETHLEY Instrument).

The XRD spectra of ZnO film were obtained by Philips diffractometer with monochromatic Cu-Kα radiation. The photo-catalytic activity of ZnO films was studied under UV irradiation using Rhodamin B dye dissolved in water. 10 ppm rhodamin B dye solution was prepared in a 100 ml beaker using de-ionized water and placed on the hot plate with stirrer in a closed chamber with UV lamp. Three samples of ZnO films (same number of layers) annealed at 400^{o}C were placed in the beaker containing rhodamin B dye and irradiated with UV light. The absorbance of the dye at the peak position after every 1h irradiation was measured using UV/VIS/NIR Spectrophotometer.

2.0 Methodology

Zinc acetate dihydrate (mol. weight: 219.50) was used as the precursor material of ZnO. The concentration of zinc acetate was 0.5 M with ethyl alcohol as a solvent and diethanolamine (DEA) was used as a stabilizer. Zinc acetate dihydrate was dissolved in ethyl alcohol under constant stirring for 2 h using a magnetic stirrer and DEA was added drop wise to get the transparent sol of ZnO at room temperature. The molar ratio of diethanolamine to zinc acetate was adjusted to 1:1. The resultant ZnO sol was stirred for 2 h to get a clear and homogeneous solution, which was stored in an air tight beaker for one day as a stock solution. Then, a few drops of the sol were placed on the pre-cleaned glass substrates and spin coated for 30 sec at 3000 rpm. As formed ZnO film was annealed in an oven maintained at a temperature of 100^{o}C for 15 min. Again the procedure was repeated using annealed ZnO film for making multi-layer ZnO films.

3.0Results andDiscussion

Fig. 1 shows the XRD pattern of single layer ZnO film annealed at 400^{o}C for 1 h in ambient air. It has been observed, the ZnO film exhibited polycrystalline wurtzite (hexagonal) structure after annealing at 400^{o}C. The intensity of the peaks increases with increasing the annealing temperature[14], which represents the enhancement in the crystallinity of the film.

The most prominent peak observed corresponds to (101) plane for 2θ =36.39^o. Other planes corresponding to (1 0 0), (002), (1 0 2), (1 1 0), etc. are also observed with relatively low intensities. The crystallite size of the ZnO film was calculated using Scherrer's method [15] and found to be 21.6 nm (for 101 orientations).

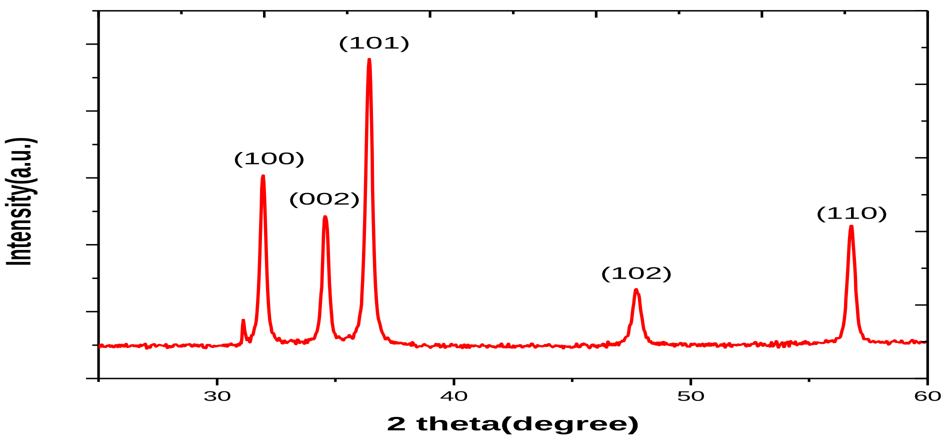

Fig.1: XRD pattern of single layer ZnO film annealed at 400^{o}C for 1 h in air.

Fig. 2 shows the optical transmittance spectra of multi-layer ZnO films deposited on glass substrates and annealed at 100°C for 15 min. It has been observed that the optical transmittance of single, double and triple layer ZnO film was almost same with an average transmittance of 87 % in the visible region. However, the optical transmittance decreased with increasing the number of layers to four and five with an average transmittance of 83 and 82 %, respectively in the visible region.

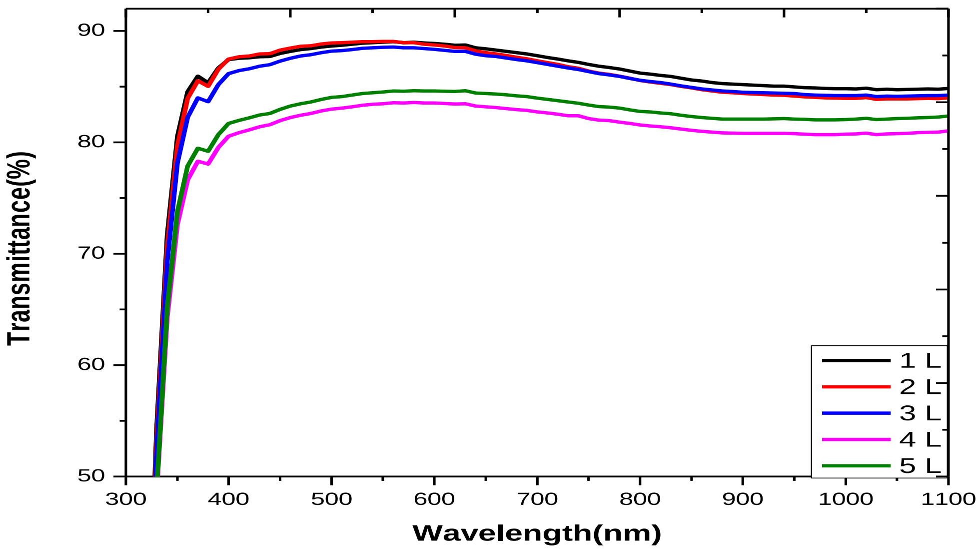

Fig. 2: Optical transmittance spectra of multi-layer ZnO thin films annealed at 100°C in air.

The optical transmittance spectra were used to find the optical band gap energy of ZnO film by Tauc method [16, 17]. A plot of $(\alpha h\upsilon)^2$ versus photon energy (hυ) in eV was plotted for each layer of ZnO film and the optical band gap energy was estimated by extrapolating the straight line towards x-axis. The estimated band gap energies were decreased from 3.46 to 3.35 eV with increasing the number of layers of ZnO from 1 to 5, respectively, as shown in the Fig. 3. The decrease in band gap energy with annealing temperature is due to the change in the morphology of the film. The band gap energy also varies with the doping of other materials [18].

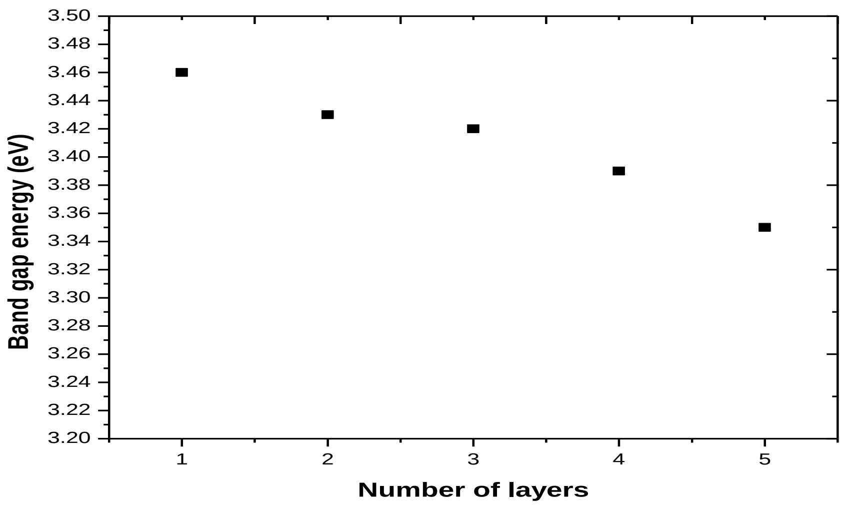

Fig. 3: Variation of optical band gap energy of ZnO film with number of layers.

The electrical resistivity of the ZnO film varied with distance on the surface of glass substrate. The average resistivity of the ZnO film was calculated for each layer of ZnO film annealed at 400°C for 1 h in air. The resistivity decreased from 5.76 x 10^6 ohm-m to 3.05 x 10^6 ohm-m with increase of number of layers from 1 to 5, as shown in the Fig. 4.

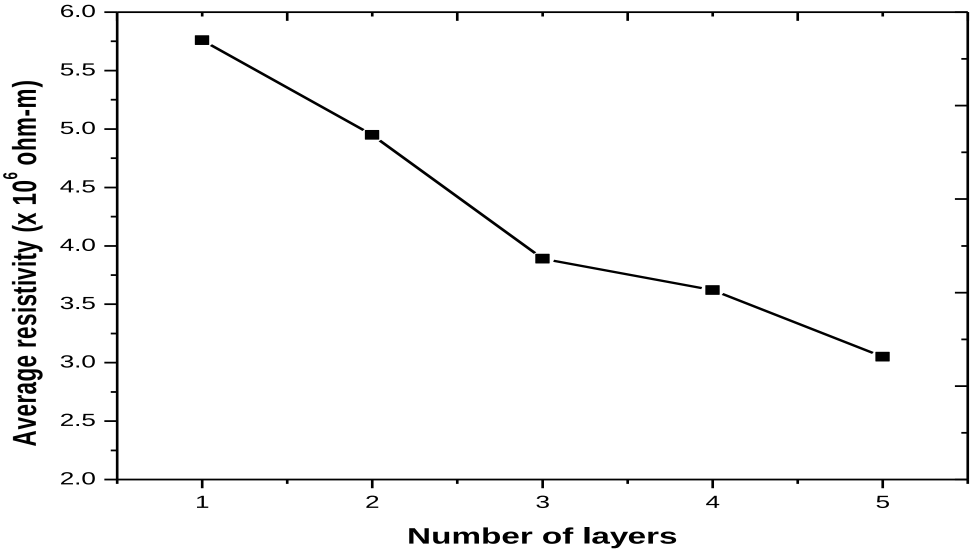

Fig. 4: Variation of average resistivity of ZnO film with number of layers.

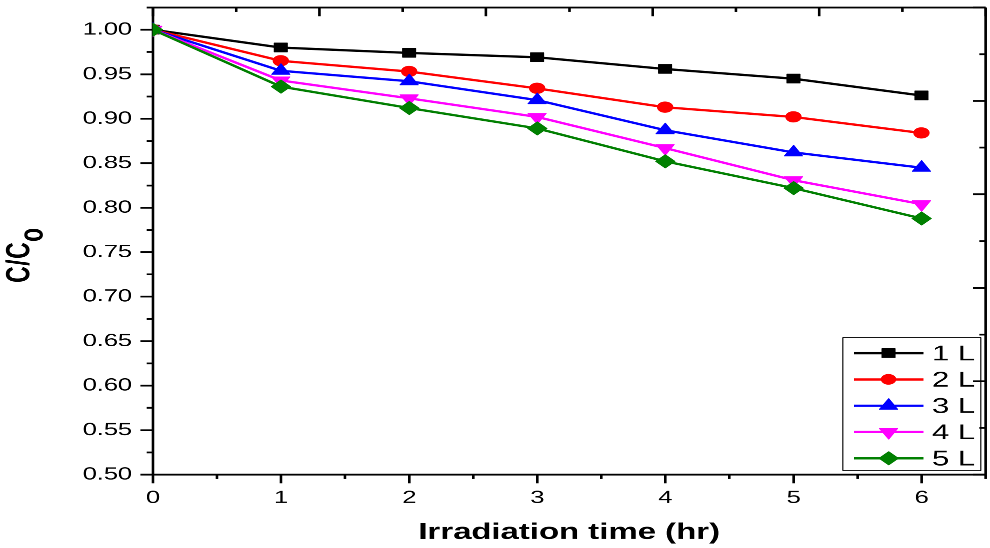

Fig.5: Photo-catalytic degradation of rhodamin B dye using multi-layer ZnO films.

Fig. 5 shows the photo-catalytic degradation of rhodamin B with time in presence of UV light using multi-layer ZnO films annealed at 400°C in ambient air for 1 h. The photo-catalytic degradation of organic dyes follows Langmuir–Hinshelwood kinetics [19]. This type of photo-catalytic reaction can be represented as follows [20,21]:

$\ln (C/Co) = - kt$

where k is a constant, Co and C are the initial concentration of rhodamin B at time t =0 and the concentration at the irradiation time t > 0 (h), respectively.

It has been observed that, the photo-catalytic activity increased with increasing the number of layers of ZnO and is maximum for 5 layer ZnO film. It may be due to the increase of concentration of ZnO with increasing the number of layers.

4.0Conclusion

The transparent and optically smooth multi-layer ZnO thin films were successfully synthesised by the sol-gel method. The structural studies reveal the hexagonal wurtzite structure after annealing at 400°C in air. Optical band gap energy is decreased and electrical resistivityis increasedwith increasing the number of layers of ZnO film. The films exhibited good photo-catalytic activity with increasing the number of layers of ZnO film.

Acknowledgements

The authors are thankful to Dr K. Narasimha Rao, Chief Research Scientist (Retd), Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore, India for his valuable information and support for this work.

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