INDUSTRIAL PURPOSE HIGHLY TRANSPARENT AND LOW RESISTIVE SYNTHESIS OF WELL ORIENTATED B:ZnO THIN FILMS

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ABSTRACT

The doping of Boron by facile, novel, newly fabricated spray CVD technique offers an ideal system to explore the effect of dopants into ZnO matrix. It yields highly transparent, conductive and quality films as the deposition process is analogous to aerosol assisted chemical vapor deposition rather than droplet deposition by spray pyrolysis technique. The properties of these thin films are governed by the additives of Boric Acid in non-aqueous solution of Zinc Acetate as a starting material. The influence of doping concentration in the range of 0.2 at% to 1 at% in steps of 0.2 on the crystalline structure and orientation of ZnO thin films have been investigated by X- ray diffraction (XRD) technique. The surface morphology and topography of these films have been characterized by FESEM and AFM techniques. The result of this study is to provide insight into the transition of triangular shaped pyramidal morphology of undoped ZnO to nanospherical, nanobeads shaped morphology whose role is played by Boron dopants into ZnO lattice. Optical transmittance measured using a double-beam spectrophotometer reveals that the average optical transmittance of films increases with doping concentration showing maximum transparency for 0.8at% doping concentration (≈90%). The transmittance curve indicates interference fringe pattern between the wave fronts generated at the two interfaces (air and substrate). The extinction coefficient of the films is nearly equal to zero which suggests there is no absorption of light at grain boundary. Boron doping results blue shifted optical band gap. The deteriorated crystallinity by addition of Boron may cause the blue shift in optical band gap. Nevertheless, refractive index and absorption edge of the ZnO films are similar to that of single crystal ZnO. The electrical studies established that 0.8 at% of B doping was the optimum for enhancing electrical conduction in ZnO thin films showing minimum resistivity and beyond that the distortion caused in the lattice which results to lower the conductivity.

***Keywords:* Transparent, CVD Technique, X-Ray Diffraction, FESEM, AFM, Nanobeads**

I. INTRODUCTION

ZnO is one of the promising materials in the field of thin film technology. It is a very fascinating material due to its versatile applications. It is an important functional oxide with wide band gap (3.37eV), applied for short wavelength optoelectronic applications including laser development [1]. It has high exciton binding energy (60meV). It allows efficient excitonic emission at room temperature [2]. It opens the prospect of fabricating semiconductor lasers in UV spectral region. It has the unique optical and electrical properties which can be used in variety of applications, such as high transmittance conductive coating oxides for solar cell [3], SAW devices [4], gas sensors [5], UV photo detectors, laser diodes [6,7] information storage device, heat mirrors, transparent electrodes [8]. Zinc oxide has been used in medical treatment for quite number of years in China.

However, literature survey [9-13] shows that the use of intrinsic ZnO is limited due to its high or moderate resistivity coupled with poor dc conductivity. Therefore polycrystalline ZnO films have been doped with group VII or group III metal ions such as indium [14], aluminum [15], gallium [16] copper (Cu), cadmium (Cd) etc. to enhance their structural, optical and electrical properties. Based on many reported investigations Boron seem to be very successful element due to various advantages like the ionic radius of B^{3+}(0.23 Å) ions is closer to that of Zn^{2+}(0.74 Å)ions. Hence these ions are readily incorporated into the ZnO lattices by substitution. Also, the band gap of films can be easily tuned from 3.3 to 4.0 eV by adjusting B content.

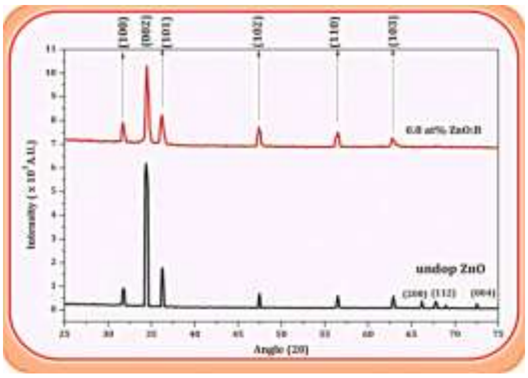
Furthermore, various research groups have been synthesized B doped ZnO thin films for different techniques such as Sylvie Faÿ et al. have synthesized rough textured Boron doped ZnO thin films by LP-CVD [9], Boen Houng have reported growth properties of sol-gel prepared ZnO:B thin films [10], B. N. Pawar al reported chemical spry pyrolysis method [11]. In this study, we have focused on the synthesis of Boron doped ZnO thin films deposited by using newly fabricated spray CVD technique at low substrate temperature.

II. EXPERIMENTAL

A 0.075M solution of Zinc acetate dihydrate in methanol, at 200 ml was used as the main solution. Boric acid was used as a dopant source with varied concentration ranging from 0.2at% to 1 at% in steps of 0.2. Compressed air having constant flow rate of 10 lpm was used as a carrier gas with constant solution flow rate of 6ml/min. Preheated glass substrates kept at low temperature offers initial nucleation growth for deposition of thin film. During deposition the reaction chamber temperature 330°C, substrate temperatures 200°C were kept constant. The crystallinity of as deposited thin films was investigated by using a Bruker AXS X-ray diffractometer. A double-beam spectrophotometer (Shimadzu UV-1800model), with an uncoated substrate in the reference path of the beam was used for optical measurement of thin films in the spectral range of 290–1100 nm. Van der Pauw Hall effect set up supplied by Scientific Equipments, Rookie, India was used to measure electrical resistivity of thin films provided with colloidal silver paste for ohmic contacts. Photoluminescence spectra of the samples were recorded with a spectrofluorimeter JASCO, model –F.P.-750, Japan using a 325nm line of an ultraviolet lamp as an excitation source.

III. RESULTS AND DISCUSSION

3.1 Structural Properties



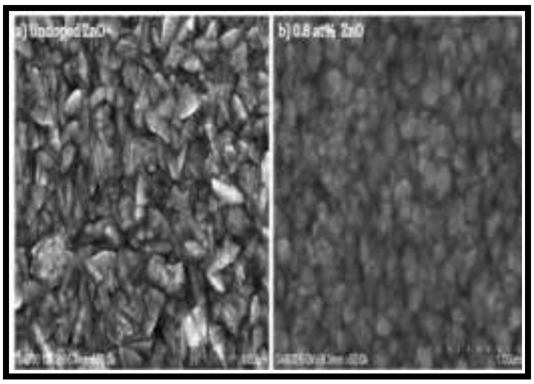
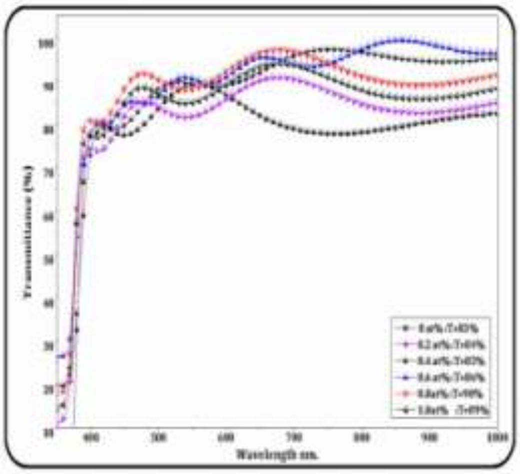


Fig. 1 XRD pattern of undoped & B: ZnO thin films Fig. 2 FESEM micrographs of undoped & B:ZnO thin films

Fig. 1 shows the key role played by different doping concentration of boron in the structural growth of ZnO thin films. Compared to JCPDS card file no. 80-0075, the XRD patterns of all the samples indicated enhanced intensities for the (002) plane, indicating preferential orientation along the c-axis. The maximum peak intensity for 0.8 at% concentration indicates optimum doping concentration. The crystallite size (D) in the films has been calculated according to the Scherrer equation. It shows that the increase of the boron content deteriorates the crystallinity resulting into the decrease in size of these grains.

The FESEM morphologies (fig. 2) of ZnO nanocrystals exhibited striking dependence on the concentration of dopants ions with transition of shapes from triangular columnar pyramids to cluster of islands, nanospheres, and finally into petal shaped morphology and conferred deteriorated crystallinity due to doping.

3.2 Optical Properties



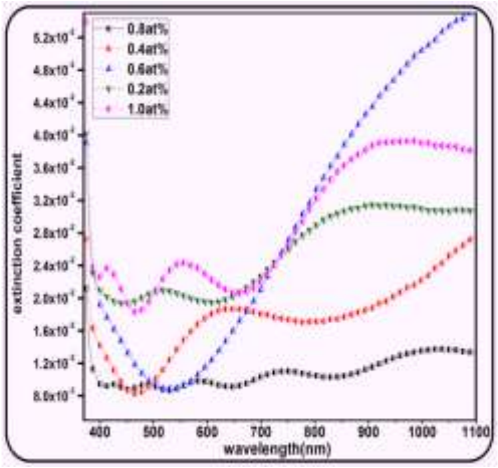


Fig.3 Transmittance of B: ZnO thin films **Fig. 4 Variation of Extinction Coeff.**

Fig. 3 represents the optical transmission of the Boron doped ZnO thin films. The maximum visible average transmission was found to be 90% for 0.8at% Boron doping in ZnO thin films. It shows that increasing doping concentration, results into increased transmittance of thin films. The transmittance curves with variation of Boron doping concentration in ZnO thin films show interference fringe pattern between the wave fronts generated at the two interfaces (air and substrate). The pattern defines sinusoidal behavior of the curves. This revealed the smooth reflecting surfaces of the film and there was not much scattering/absorption loss at the surface suggesting that it has non uniform distribution of film thickness, refractive index and conductivity.

From the transmittance and absorbance spectra the corresponding reflectance (R) values can be calculated by the relation,

$$R = \frac{(1+n)^2}{(1-n)^2} \quad \text{---------------[1]}$$

where n is refractive index. The variation of extinction coefficient and refractive index is as shown in figure 4 & 5 respectively. The extinction coefficient is nearly equal to zero indicating very low absorbance. The refractive index increases with increase in Boron doping and is maximum for 0.8at% doping concentration.

Fig. 6 shows the variation of optical band gap (Eg) of Boron doped ZnO thin films deduced from the photon energy dependence of the absorption coefficient. Boron doping results blue shifted optical band gap from 3.25eV of undoped

ZnO to 3.30 eV for optimized doping concentration of 0.8at%. The deteriorated crystallinity by addition of Boron may cause the blue shift in optical band gap

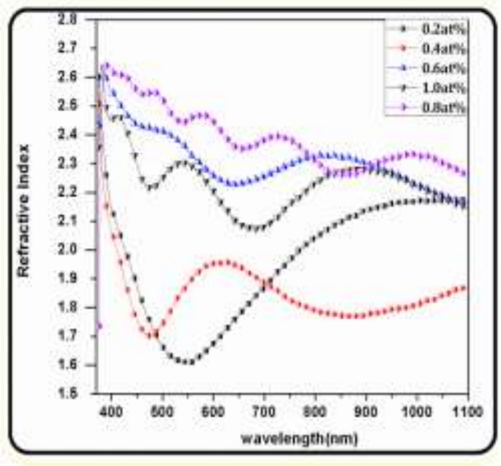


Fig. 5 Variation of Refractive Index

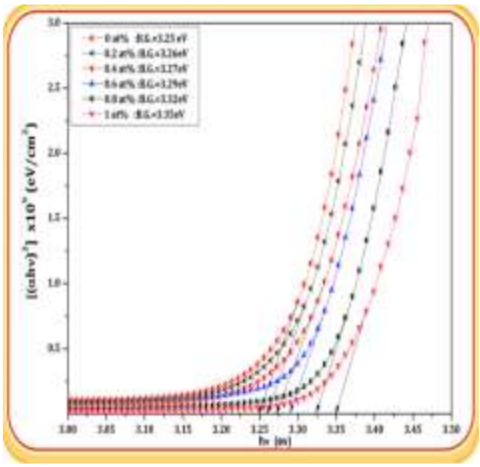


Fig. 6 Band gap of B:ZnO thin films

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3.3 Electrical Characteristics

Fig.7 shows Arrhenius plot of Log (ρ) versus 1000/T for Boron doped ZnO thin films synthesized by spray CVD technique. The plot shows two types of conduction regions: (i) an exponential fall region and (iii) saturation region. It also shows decrease in resistivity with temperature indicating semiconducting behavior. At higher temperature the adsorbed oxygen molecules are desorbed from the surface of thin film, hence potential barrier at grain boundaries decreases which causes the electrons to cross grain boundaries. It also affects to increase donor densities due to thermal excitation.

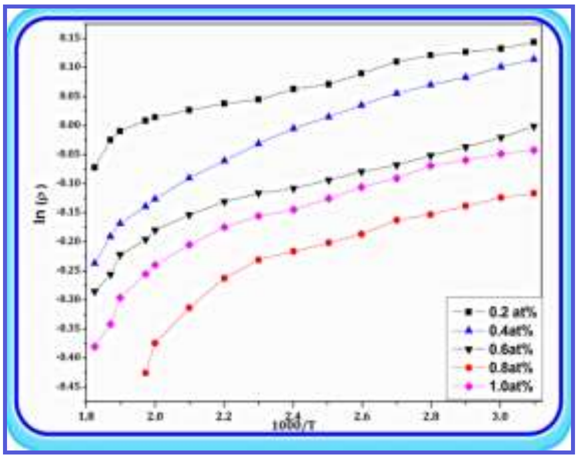

Fig.7 Arrhenius Plot for B :ZnO thin films

Van der Pauw resistivity and Hall effect measurements are used to measure the electrical parameters [such as the sheet resistance (Rs), resistivity (ρ), carrier concentration (n), and mobility (μ)] as the function of Boron doping concentration. Both the sheet resistance and resistivity are found to decrease with increasing doping concentration. On the other hand, Hall mobility and the carrier concentration increase resulting to decrease the resistivity. From the Hall Effect measurements, it was observed that the Boron doped ZnO films exhibit n-type conductivity.

Table 1 Hall Effect Measurements

Sample	Resistivity	Conductivity	Carrier Conc.	mobility
at%	Ω.cm	$(\Omega.cm)^{-1}$	cm^{-3}	$cm^2/V.s$
0.2	$4.7x10^{-2}$	21	$4.2\ x10^{19}$	3.2
0.4	$3.9x10^{-2}$	34	$5.9\ x10^{19}$	3.6
0.6	$2.3x10^{-2}$	42	$8.5\ x10^{19}$	3
0.8	$7.7x10^{-3}$	129	$1.5\ x10^{20}$	6
1.0	$1.9x10^{-2}$	52	$8\ x10^{19}$	4

IV CONCLUSION

B doped ZnO thin films have been successively deposited at low substrate temperature by spray CVD technique. XRD spectra reveal deteriorated crystallinity induced by Boron doping. The FESEM micrographs show similar behavior. Optical transmittance spectra indicates that 0.8 at% doping concentration reveals highly transmittance in the visible region. It also shows lowest resistivity calculated from Hall Effect measurements. Hence these films show potential application towards transparent conducting oxide.

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