Effect of low to heavily boron doped pyrolized zinc oxide (ZnO:B) thin films

U R Dash¹, M K R Khan¹, M M Rahman¹ and M Kamruzzaman²

¹Department of Physics, University of Rajshahi, Rajshahi-6205
²Department of Physics, Begum Rokeya University, Rangpur- 5400

E-mail: unnatiphr4337@gmail.com

Abstract. Boron doped ZnO thin films have been deposited on glass substrate at temperature (350 ± 5) °C by spray pyrolysis technique and studied structural and physical properties. XRD study reveals polycrystalline hexagonal structure. The crystallite size varies in the range 8 – 44 nm irrespective of crystal planes and doping concentration of B as well. SEM study shows the formation of nano-walls in B doped ZnO thin film. There are some voids in the film, which decreased as the B concentration increased. Temperature dependent resistivity of the films has been measured within the temperature range 300 K to 475 K for different B doped samples, which reveals the semiconducting nature of the films. Activation energies ∆E₁, varies from (0.022 - 0.035) eV in the temperature region (303 K-400 K) and ∆E₂, varies from (0.033-0.188) eV in (400 K - 475 K) depending on Boron concentrations.

1. Introduction

The interest in ZnO is renewed by its increasing demand and high prospects in optoelectronics applications because of its direct band structure, wide band gap (Eg, ≥3.34 eV at 300 K) and large exciton binding energy of ≥60 meV [1]. The exciton binding energy is 2.4 times of the thermal energy (kBT=25 meV) at room temperature (RT). Recently, several groups have carried out research on partially substituted compounds of ZnO by using various methods for improving the electrical performance. Low-resistivity n-type ZnO could be realized by doping with group IIIA [B, Al, Ga, In] elements. The Al, Ga, and In-doped ZnO thin films have been researched by various groups [2–4]. Although recent work has demonstrated the doping of these group IIIA elements onto ZnO, the formation of boron doped ZnO thin films is still difficult because of complex structure of Boron. Here, we have chosen spray pyrolysis method because pyrolysis is a convenient, low-cost, and rapid method for the deposition of thin films, and has been used for many years for the manufacture of conductive glass. It is also an excellent method for preparing films of semiconductor alloys and complex compounds.

2. Experimental Section

Undoped ZnO and ZnO:B have been deposited on ordinary glass substrate by spray pyrolysis technique at substrate temperature of 350 °C. The most commonly available microscope glass slides were used as substrates in the present work. The solution comes to the spray nozzle through a commercially available medical infusion pipe with controlling system. The deposition solution is then sprayed to the substrate by an air compressor. The working solution was prepared by mixing the appropriate volumes of 0.1M Zinc acetate (Zn(CH₃.COO)₂ 2H₂O) dehydrate and 0.1M Boric acid (H₃BO₃) dissolved in distilled water. Here Zinc acetate and Boric acid were mixed together in different
nominal volume ratios to obtain 0%, 0.2%, 0.6%, 1%, 2%, 3% and 4% Boron doped ZnO thin films. The most commonly used solvent is water. The thickness of the films was measured using Newton’s ring method. The structural properties were studied using XRD. The XRD diffraction study of undoped and B doped ZnO thin films on glass substrate has been done with a diffractometer (Model D2 PHASER (BRUKER)), using Cu-κα radiations of wavelength 1.54184 Å with tube current 10 mA and voltage 30 kV. The peak intensities are recorded corresponding to their 2θ values. The XRD data were taken in the range of 2θ = 20° to 80°, with a step size of 0.02°. The morphological studies were done using SEM. Electrical resistivity of thin films was analyzed using Van-der Pauw’s method.

3. Results and Discussion

3.1 X-ray Diffraction Study

The x-ray diffraction (XRD) patterns are shown in figure 1, which clearly show that the films are polycrystalline in nature for all compositions. The characteristic peaks were identified comparing with JCPDS card (Card no. 2100100) and these were at (2θ)° = 32.7804, 35.3642, 37.2184, 48.3863, 57.4629 and 68.7872 corresponding to the (hkl) planes (100), (002), (101), (102), (110), and (112) respectively. For all composition the possible phase is ZnO. From the XRD patterns it is also seen that the intensity of (100), (002) and (101) planes are nearly equal for undoped sample.

From XRD Pattern it is seen that the intensities of the prominent peaks (100), (002) and (101) are increased with the progression of doping concentration except for 5% doped sample. However, increased of prominent peaks are not systematic. Though there is a systematic increased of intensity of (101) planes is observed with concentration. This means that with the doping of B in ZnO, Crystalline orientation is along [101] direction except for 3% and 5% B doped sample. The intensity of 5% B doped sample is very small which indicates that this sample is poorly crystalline and may be more doping will induce amorphous nature of the sample. The crystalline orientation of 3% and 5% B doped sample is along [002] direction. This type of variation of crystal orientation may be due to the effects of doping concentration and growth temperature as well. Although, in this work a particular temperature 350 ± 5 °C was used to prepare all the films yet there was a possibility of substrate temperature variation during the growth because temperature control is not an easy task since the heat of substrate comes from cooking heater. So the variation of temperature during growth is inevitable which may change the crystal orientation. Both doping and temperature dependent crystal orientation was reported [5].

The observed peaks positions and d-spacing of the films matched only with Hexagonal ZnO structure imply that there are no secondary phases such as a Boron cluster or oxides. So it is assumed that B2+ ions replaced Zn2+ sites as substitutional atom in a wurtzite structure. The XRD pattern suggested that the obtained phases are the characteristic plane of ZnO. The d_{hkl} values were calculated using the Bragg’s law,

\[ 2d \sin \theta = n\lambda \]

where, d is the inter-planer spacing, θ is the Bragg angle and λ is the wavelength of radiation. The corresponding lattice parameters were calculated using the formula:

\[ \frac{1}{d^2} = \frac{4}{3} \left\{(h^2 + hk + l^2)/a^2 \right\} + \frac{l^2}{c^2} \]

The crystallite size was calculated by using Debye-Scherrer formula [2]:

\[ \xi = \frac{K \lambda}{\beta \cos \theta} \]

where, ξ is the Crystallite size, K is a constant whose value is 0.94, λ is the wavelength of X-ray used, β is the full width at half maxima (FWHM) expressed in radians and θ is the Bragg angle. The calculated lattice parameter, crystallite size, dislocation density and crystalline strain are given in Table 1.
Figure 1. X-ray diffraction patterns of undoped and Boron doped ZnO thin films.

Table-1: Crystal lattice parameter, crystallite size, dislocation density and crystalline strain.

| B%  | Lattice parameter (nm) | Crystallite size, $\xi$ (nm) | Dislocation density, $\delta \times 10^3$ lines/nm$^2$ | Crystal strain, $\epsilon \times 10^{-3}$ |
|-----|------------------------|-------------------------------|------------------------------------------------------|------------------------------------------|
|     | a                      | c                             | (100)       | (002)       | (100)       | (002)       | (100)       | (002)       |
| 0.0 | 0.315                  | 0.507                         | 27.45       | 18.43       | 1.33        | 2.94        | 4.671       | 6.464       |
| 0.6 | 0.320                  | 0.514                         | 24.37       | 24.54       | 1.63        | 1.66        | 5.342       | 4.918       |
| 0.8 | 0.320                  | 0.511                         | 21.94       | 27.62       | 2.07        | 1.31        | 5.931       | 4.343       |
| 1.0 | 0.320                  | 0.514                         | 27.41       | 15.77       | 1.33        | 4.02        | 7.139       | 4.759       |
| 3.0 | 0.321                  | 0.515                         | 27.40       | 13.80       | 1.33        | 5.25        | 4.771       | 8.772       |
| 5.0 | 3.188                  | 5.130                         | 21.94       | 10.04       | 2.08        | 9.90        | 5.906       | 11.989      |

3.2 Scanning Electron Microscopy study
Scanning electron microscopy (SEM) has been performed by Field emission scanning electron microscope (Philips XL30 FEG) at different magnifications to observe surface morphology and find out the existence of grain, defect, etc. From figure 2(a,b,c) it is seen that poorly dense nanowalls are randomly distributed over the surface. These nanowalls contain small particles with some voids as observed on the nanowalls. As the B concentration increases small particles are uniformly distributed over the surface and the voids are decreased (shown in figure 2(d,e,f)). For 5% B doped sample small particles are distributed in such a way that they make big circles over the surface. Within the circle it is seen that semispherical particles are distributed over the surface (shown in figure 2(g,h,i)).
Figure 2. SEM micrographs of 1% (a,b,c), 3% (d,e,f) and 5% (g,h,i) boron doped ZnO.

3.3 Electrical Properties
Variation of resistivity and conductivity with temperature for undoped and Boron doped ZnO thin films are measured by Vander Pauw’s [6] method in air ambient in the temperature range (300 K - 475 K). From figure 3(a) it is observed that the resistivity decreases with increasing temperature, which is a general feature of a usual semiconductor; both for undoped and Boron doped ZnO thin films. The resistivity was lowest for undoped ZnO thin films which increased with increasing doping concentration of boron. From the figure it is also observed that the room temperature resistivity increases with doping concentration. It is well known that the radius of B is smaller (0.88 Å) compared to Zinc atom (1.33 Å), so during the crystallization it may occupy partially at interstitial position along with substitutional solid solution. Furthermore, it may take the position in grain boundary. Therefore, with boron doping RT resistivity may increase. Conductivity increases with the increase of temperature as shown in figure 3(b). Form this figure it is also seen that conductivity decreases with increasing B doping concentrations.
3.4 Activation Energy

The activation energy can be calculated from the equation

\[ \sigma = \sigma_0 e^{-\Delta E/2k_B T} \]  

(4)

For the calculation of activation energy, \( \Delta E \), the \( \ln\sigma \) versus \( 1/T \) curves for Boron doped ZnO thin films are drawn in figure 4. The activation energies of the films have been calculated from the slopes of the curves. The activation energy of the films is estimated from two regions, \( \Delta E_1 \) for low (303 K-400 K) temperature region and \( \Delta E_2 \) for high (400 K-475 K) temperature region. These values are given in Table 2. From the table it is observed that the activation energy \( \Delta E_2 \) is higher than that of \( \Delta E_1 \). The values indicate that conductivity is associated with the impurity band transition of carriers i.e. from donor level to conduction band and the low values of \( \Delta E_1 \) may be associated with the localized levels hopping due to the excitation of carriers from one defect state to other.

Figure 3. Variation of resistivity and conductivity with temperature for Boron doped ZnO films.

Figure 4. Variation of \( \ln\sigma \) with \( 1/T \) for Boron doped ZnO thin films.
Table 2. Activation energies evaluated for undoped and Boron doped ZnO thin films.

| Sample         | % of Boron | Activation energy, $\Delta E_1$(eV) | Activation energy, $\Delta E_2$(eV) |
|----------------|------------|-------------------------------------|-------------------------------------|
| B doped ZnO    | 0          | 0.022                               | 0.033                               |
|                | 0.2        | 0.032                               | 0.002                               |
|                | 0.6        | 0.106                               | 0.024                               |
|                | 1          | 0.112                               | 0.172                               |
|                | 3          | 0.035                               | 0.188                               |

3.5 Study of Hall Coefficient, Hall Mobility and Carrier Concentration

The Hall voltage measurement was done at room temperature and at constant magnetic field of 9.815KG. From the Hall voltage measurement, Hall constant ($R_H$), Hall mobility ($\mu_H$) and carrier concentration (n) have been calculated and are tabulated in Table 3. It is seen that Hall coefficient increases with increasing doping concentration of B. The carrier concentration n and conductivity decreases with increasing doping concentration. The calculated values of carrier concentrations belonging to these films are found to be the order of $\sim 10^{16}$. From figure 5 we see that carrier concentration and mobility decreases whereas resistivity increases with increasing B concentration.

Figure 5. Variation of resistivity, carrier concentration and Hall mobility with Boron concentration.

Table 3. Hall constant ($R_H$), Hall mobility ($\mu_H$), carrier concentration (n) and conductivity (\(\sigma\))

| Doping concentration (B %) | Hall coefficient, $R_H$ (cm$^3$/coul) | Type | Hall mobility, $\mu_H$ (cm$^2$/Vsec) | Carrier concentration, n $\times 10^{16}$ (cm$^3$) | Room temperature conductivity, $\sigma$ (mho-cm$^{-1}$) |
|----------------------------|----------------------------------------|------|--------------------------------------|-----------------------------------------------|----------------------------------------------------|
| 0.0                        | -5.51                                  | n    | 28.87                                | 1.43                                          | 5.24                                               |
| 0.2                        | -5.93                                  | n    | 27.81                                | 1.15                                          | 4.69                                               |
| 0.6                        | -6.82                                  | n    | 20.11                                | 1.02                                          | 2.95                                               |
| 1.0                        | -8.02                                  | n    | 15.32                                | 0.85                                          | 1.91                                               |
| 3.0                        | -10.16                                 | n    | 13.41                                | 0.51                                          | 1.32                                               |

ZnO and B doped ZnO thin films are deposited by spray pyrolysis method. The deposited films are polycrystalline with hexagonal structure as confirmed by XRD experiment. The preferred crystallographic orientation of ZnO in (002) plane changed to (101) by doping concentration of B.
The SEM micrograph confirms small particles with some voids as observed on the nanowalls. Hall measurements of the B doped ZnO films were carried out at room temperature, which confirmed that the undoped and B doped ZnO thin films are n-type semiconductor. The carrier concentration was found to decrease with increasing doping concentration of B and the carrier concentration was found to the order of $\sim 10^{16}$ cm$^{-3}$.

Acknowledgement
One of the authors Unnati Rani Dash is thankful to the Ministry of Science and Technology (MOST) of the Peoples Republic of Bangladesh for providing financial support.

References
[1] Liang W Y and Yore A D 1968 Phys. Rev. Lett. 20 59
[2] Wang R, Sleight A W and Cleary D 1996 Chem. Mater. 8 433
[3] Ambrosini A, Malo S and Poeppelmeier K 2002 Chem. Mater. 14 58
[4] Palmer G B, Poeppelmeier K R and Mason T O 1997 Chem. Mater. 9 3121
[5] Liton M N H, Khan M K R, Rahaman M M and Islam M M 2015 Journal of scientific research 7(1-2) 23
[6] Öztas M and Bedir M 2008 Thin Solid Films 516 1703