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Comparison of structural, optical and electrical properties of undoped and boron doped ZnO thin films for varying thickness deposited by advanced spray pyrolysis technique at low substrate temperature

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ABSTRACT

Thickness varied thin films of undoped and Boron doped Zinc oxide have been prepared on glass substrates by advanced spray pyrolysis techniques at low substrate temperature (200°C) using different volumes of 0.075M non-aqueous solution of Zinc acetate and boric acid for doping. The structural, optical and electrical properties of undoped zinc oxide (ZnO) thin films of various thicknesses were compared with those of B-doped (BZO) thin films. Transparent, high-quality undoped ZnO and BZO films were deposited successfully using advanced spray pyrolysis technique at low substrate temperature (200°C). The films were polycrystalline with a hexagonal structure and a strongly preferred orientation along the c-axis. X-ray diffraction analyses showed that the crystallinity of BZO films were deteriorated by addition of boron as compared to undoped thin films. Moderately high average optical transmittance has been observed for doped films than undoped films in the visible part of the electromagnetic spectrum. Blue shift in optical band gap is observed due to doping. Enhanced electric conductivity is observed for BZO thin film as compared to undoped films of different thickness.

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KEYWORDS

Zinc oxide thin films;
B-doping;
Advanced spray pyrolysis;
Electrical properties;
Optical properties;
Structural properties.

INTRODUCTION

Zinc oxide (ZnO) is one of the most prominent metal oxide semiconductors. It is an n-type semiconductor of hexagonal (wurtzite) structure with a direct energy wide band gap of about 3.37eV at room temperature. It is a versatile material with good electrical and optical properties, thermal and chemical stability. It is abundant in nature, low-cost and non-toxic. Due to this versatility

ZnO has drawn considerable attention. It has been find a multitude of immensely important applications in electronic and optoelectronic devices such as transparent conductors, solar cell windows, gas sensors, surface acoustic wave (SAW) devices, heat mirrors etc^[1-5]. It is also being considered as a potential candidate in the new frontiers of research like spintronics^[6]. Extensive studies have been made on the structural and optical properties of ZnO thin films grown by various tech-

niques^[7-9].

Doped and undoped ZnO thin films are currently under intense investigation and development for optoelectronic and energy conversion applications. In particular, transparent and conductive B:ZnO(BZO) films are being considered for manufacturing transparent electrodes in flat panel displays, solar cells and organic light-emitting diodes due to their high electro optical quality, high material availability and low material cost for large area applications^[10-12].

The electrical resistivity of ZnO thin films decreases by doping it with positive trivalent atoms such as (Al, Ga, In, B) at cationsite^[13, 14]. The incorporation of B in ZnO showed improvement and stability of conductivity of ZnO:B films. Among the processes used to prepare undoped & BZO coatings, advanced spray pyrolysis is considered to be a suitable technique due to its inherent characteristics such as high deposition rate, good controllability and scalability to large areas. In advanced spray pyrolysis technique, basic structure of the system is completely changed. In this system, nozzle is fixed and placed at inferior (below) position and complete reaction of decomposition takes place in the reaction chamber, only the final product in the vapors form can be deposited on the substrates which are kept at a low temperature. With the help of this system we have successfully deposited FTO thin films^[15].

Several studies have been done for the interrelation between the structural, optical and electrical characteristics of undoped ZnO and BZO layers. Besides, it should be noted that for the same temperature and atmosphere, the layer properties can also be dependent on the film thickness. In general, the mean crystallite size is found increasing and the gap energy decreasing as the film thickness increases. Thus, it is important to know how the undoped and BZO layer properties are affected by the film thickness.

In this work, the undoped and BZO thin films with various thicknesses have been deposited by advanced spray pyrolysis at room temperature. Then, they have been analyzed comparatively by structural, optical and electrical measurements. The objective is to get a better understanding of the relationships between the different characteristics of the undoped and BZO layers and their dependence on the film thickness. This will contribute to optimize the electro optical quality of the

material as transparent and conductive electrode.

EXPERIMENTAL PROCEDURE

The films of ZnO and B:ZnO were deposited on glass substrates by advanced spray pyrolysis technique. It is a very simple and relatively cost-effective method for preparing films of any desired composition under controlled conditions, involving the spraying of a solution containing a soluble salt of the cation of interest on to a heated substrate. The details of film deposition has been reported elsewhere^[15].

In the present investigation the ZnO & B:ZnO thin films were deposited on properly cleaned glass substrates, all having 2.5cm × 1cm dimension. The precursor solution used was of 0.075M concentration of high purity zinc acetate dehydrate (AR grade Thomas Baker, India) prepared in methanol (CH₃OH). Boric acid (AR grade Thomas Baker, India) was used as the source of dopant. The dopant concentration of Boron (B/Zn at%) was 0.75at% prepared for different solution quantity. All the undoped and B-doped ZnO thin films of five different thickness were prepared separately for different solution quantity under the same parametric conditions, as given in TABLE 1. The detailed description of the spray system is given in^[15]. During optimization of the process parameters for preparing ZnO & B:ZnO thin films, the substrate temperature was found to be the most important parameter influencing the film properties. To obtain good-quality ZnO & B:ZnO thin films, suitable for transparent conducting studies, the optimized value of substrate temperature was found to be 200°C. In the present investigation the substrate temperature was therefore kept at a constant value of (200 ± 10)°C. Film thickness was determined by surface profiler model Ambios XP-1. The tempera-

TABLE 1 : Deposition conditions for ZnO & B:ZnO

Parameter	Value
Substrate temperature(Ts)	220°C
Reaction chamber temperature	330°C
Air flow rate	10 LPM
Spray Rate	6ml/min.
Zinc acetate concentration	0.075M
Boron doping concentration	0.75%
Sprayed quantity	100 to 500ml

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ture was monitored during the entire deposition process using a chromel-alumel thermocouple with the help of PID temperature controller. The structural characterization of the films was performed using a Bruker AXS X-ray diffractometer with phase identification using PAnalytical X'Pert HighScore with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The diffraction angle ' 2θ ' was varied from 30° to 100° with a step of $0.02^\circ/\text{min}$. For electrical characterization, high conducting silver paste was used to make ohmic contacts on both ends of the ZnO thin films. The contacts were properly placed and allowed to dry. The films were mounted on a two-probe assembly. The temperature of the film was varied from room temperature (20°C) to 500°C in steps and allowed to equilibrate for some time at intervals of 10°C . At each stable temperature, the electrical resistivity of the film was obtained from the resistance measurements performed using a digital multimeter. The optical transmission spectra for undoped and B-doped ZnO thin films were obtained in the ultraviolet (UV)/visible/near-infrared (NIR) region from 200 to 1100nm using UV-VIS spectrophotometer (Shimadzu 1800 model). The measurements were carried out in the wavelength scanning mode for normal incidence at room temperature using an uncoated glass slide as reference.

RESULT & DISCUSSION

Non-aqueous solution of zinc acetate dissolved in methanol, when sprayed over the preheated substrates through the reaction chamber, pyrolytic decomposition of solution takes place and constituent reacts to result into zinc oxide. The possible chemical reaction of ZnO film formation from zinc acetate solution as follows^[16],

$$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 2\text{CH}_3\text{OH} \rightarrow \text{ZnO} + 2(\text{CH}_3\text{COCH}_3) + 3\text{H}_2\uparrow + \text{O}_2\uparrow$$

The films deposited onto the amorphous glass substrates were mirror smooth, uniform and well adherent to the substrate. For Boron doping, the corresponding quantities of 0.8at% Boric acid (H_3BO_3) dissolved in methanol were added to the main solution.

Figure 1 shows thickness variation of undoped and Boron doped ZnO thin films. From Figure 1 it is observed that doping of boron causes to increase thickness of thin film^[17]. According to B.J.Lokhande this may be due to difference in ionic radius of boron and Zinc.

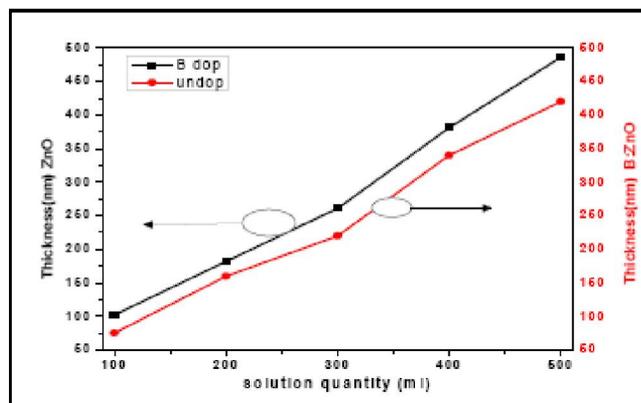


Figure 1 : Variation of film thickness

Ionic radius of boron is smaller than zinc therefore, ionic bonding between Boron and oxygen is stronger compared to the ionic bonding between zinc and oxygen. This strong bonding between boron and oxygen reduces the rate of evaporation and results in increase in thickness of thin film.

Structural characterization

The X-ray diffraction spectra for comparison of undoped ZnO and B:ZnO thin films prepared by advanced spray pyrolysis technique at low substrate temperature for variation of thickness are shown in Figure [2.1] and [2.2]. The following observations have been made from the X-ray diffraction spectra of both films. It shows that both undoped and B:ZnO thin films are polycrystalline. All the diffraction peaks in both patterns for all range of thickness variation correspond to the reflection of a hexagonal wurtzite-structured with preferential orientation along the c-axis perpendicular to the substrate surface [JCPDs No.(PDF) 80-0075]. The position of the measured diffraction peaks and the growth orientations are independent of the film thickness. But the intensities of the peaks, especially the (002) peak increases with increasing the film thickness for both undoped and Boron doped ZnO thin film. This signifies that the improvement in crystallinity with increase in film thickness.

As compared with B doped thin film, undoped ZnO thin films reveals greater intensities for (002) plane. Hence Boron doping affects crystallinity of thin film. Hu and Gordon reported that gallium doped ZnO films have less orientation along the c-axis^[18]. It suggests that, there is some kind of diffusion barrier to accumulate interstitial additional Boron atoms in ZnO matrix to maintain

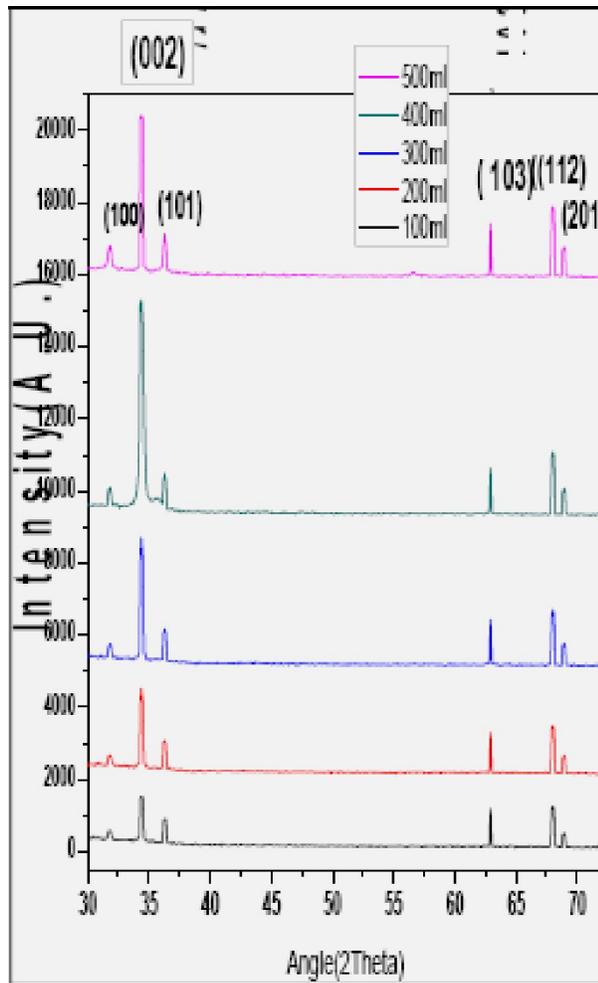


Figure 2.1 : XRD ZnO

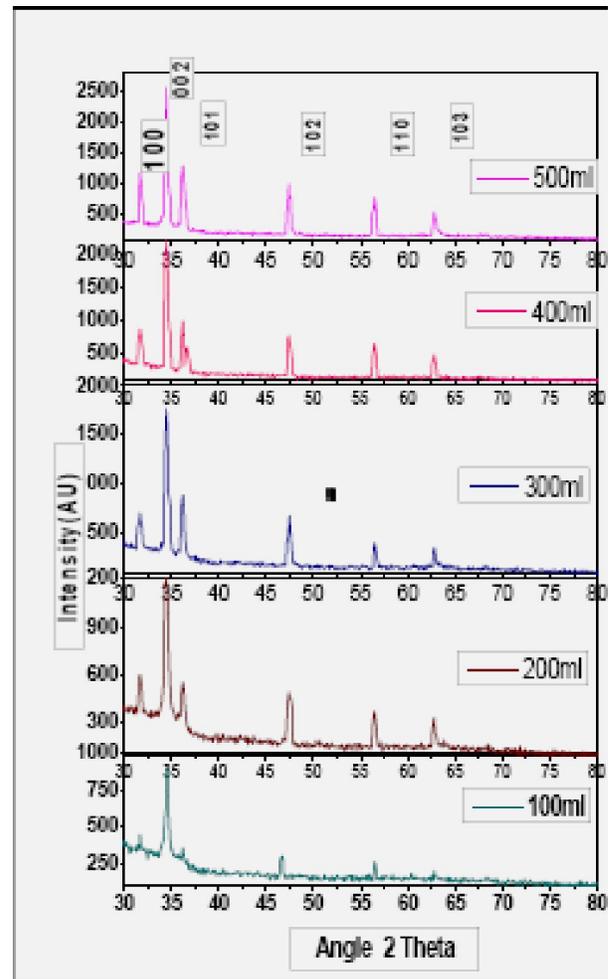


Figure 2.2 : XRD B: ZnO

unidirectionality and structure

Interestingly it is to be noted that the comparatively weak reflections (112) and (201) appeared in undoped ZnO thin films which were absent in Boron doped thin films. On the other hand, reflections (102) and (110) newly appeared for Boron doped thin films. As compared to undoped ZnO thin films, the weak reflections (100) and (101) have relatively intense peaks in B:ZnO thin films. and (103) have relatively intense peak in undoped ZnO. Except this, no remarkable change in intensity of other reflections was observed.

In order to obtain more structural information, the average crystallite size (D) for both undoped and doped ZnO thin films have been calculated using Debye-Scherrer's formula^[19].

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (1)$$

where λ , θ , and β are the X-ray wavelength

(1.54184\AA), the Bragg diffraction angle, and the full-width at half maximum (FWHM) of ZnO (002) peak, resp. In addition, to get more information on the amount of defects in the films the dislocation density was calculated using the formula^[20].

$$\delta = \frac{1}{D^2} \quad (2)$$

Using (002) peak, the estimated crystallite size, FWHM, texture coefficient are mentioned in TABLE [2.1] and [2.2] for both undoped and Boron doped thickness varied ZnO thin film. It is evident from TABLE that undoped thin films have bigger crystallite size and smaller values of FWHM and dislocation densities than BZO thin films. This implies the better crystallization of undoped thin films than BZO thin films. Quantitative information concerning the preferential crystal orientation can be obtained from the texture coefficient, T_c , defined as^[21],

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TABLE 2.1 : Structural characterization undoped ZnO

Solu tion quan tity	Thic kne (nm)	Roug. (nm)	FW HM (De gree)	Grain size (nm)	Dislo cation density (nm) ⁻²	Text ure coeff.
100ml	75	28	0.36	26.74	1.39×10^{-3}	1
200ml	160	39.3	0.3134	30.70	1.061×10^{-3}	1
300ml	220	60.1	0.3032	31.75	9.92×10^{-4}	2.25
400ml	340	102.4	0.2961	32.48	9.47×10^{-4}	2.21
500ml	420	124.7	0.2952	32.63	9.39×10^{-4}	1.959

TABLE 2.2 : Structural characterisation B: ZnO

Solu tion quan tity	Thick ne (nm)	Roug. (nm)	FW HM (De gree)	Grain size (nm)	Dislo cation density (nm) ⁻²	Tex ture coeff.
100ml	102	38	0.42611	19.5158	2.6255×10^{-3}	0.93705
200ml	182	59.3	0.40985	20.29	2.429×10^{-3}	0.9581
300ml	261	90.1	0.40687	20.438	2.3939×10^{-3}	1.1287
400ml	381	132.4	0.39404	21.099	2.2463×10^{-3}	1.5145
500ml	486	140.7	0.383047	21.705	2.1226×10^{-3}	1.8931

$$T_c(\text{hkl}) = \frac{I(\text{hkl})/I_0(\text{hkl})}{(1/N) \sum I(\text{hkl})/I_0(\text{hkl})} \quad (3)$$

where $T_c(\text{hkl})$ is the texture coefficient, $I(\text{hkl})$ is the XRD intensity and N is the number of diffraction peaks considered. $I_0(\text{hkl})$ is the intensity of the XRD reference of the randomly oriented grains. From TABLE [2.1] & [2.2] it is observed that texture coefficients of (002) plane for undoped thin films have moderately high values than Boron doped thin films. For 100 and 2000ml sol quantity, $T_c = 1$ for undoped thin film & it is nearly equal to one for doped thin films. This shows that, the films are with a randomly oriented crystallite similar to the JCPDS reference. But for above 200ml solution quantity it is greater than one which indicate the abundance of grains in a given (002) direction.

Optical absorption studies

Figure [3] & [4] represents the UV-visible transmission spectra of undoped & B:ZnO thin films recorded

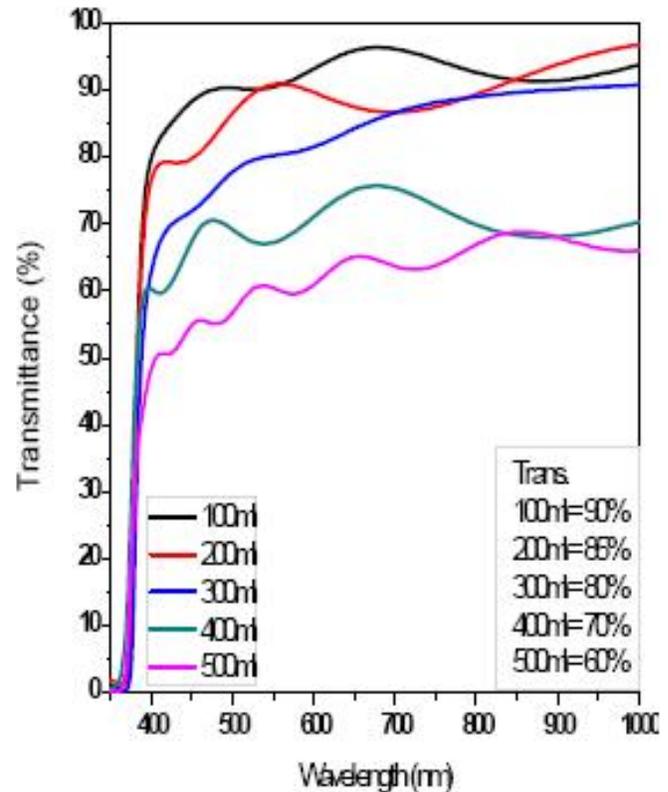


Figure 3 : Transmittance for 0.075M ZnO

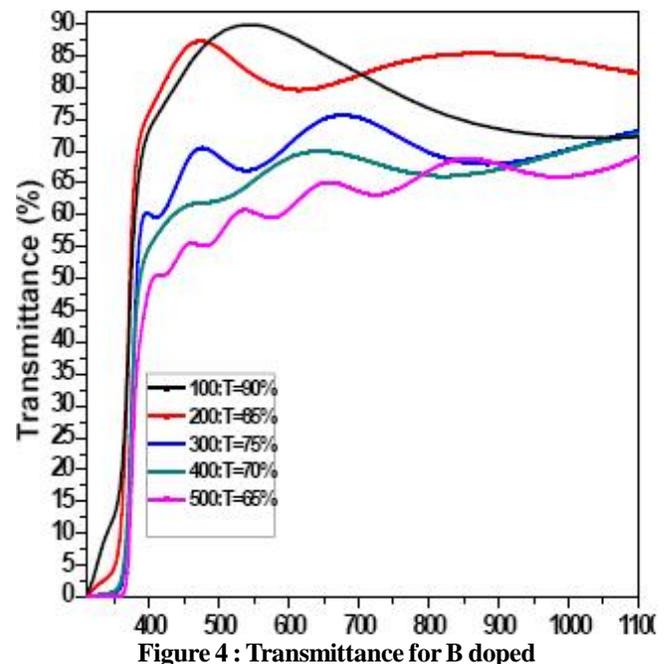


Figure 4 : Transmittance for B doped

in the visible region of 350–1100 nm, as a function thickness of thin film. The sharp fall of transmittance near the absorption edge ($\sim 350\text{nm}$) observed for all the films indicates their good crystalline and direct band gap nature. Herein, less thickness films were found to be highly transparent in the visible wavelength region. Average

TABLE 3.1 : Optical & electrical characterization undoped ZnO

Solution quantity	Avg. trans.(%)	B.G.(ev)	Sheet Res. (K.Ω)/cm ²	Fig.of merit 10 ⁻⁶ (Ω) ⁻²	Activation energy (ev)	
					E1ev 300-400 ⁰ K	E2ev 400-500 ⁰ K
100ml	90%	3.29	300	1.16	1.59	1.7
200ml	85%	3.25	220	0.89	1.23	1.55
300ml	75%	3.24	180	0.310	1.1	1.34
400ml	65%	3.22	120	0.12	0.98	1.05
500ml	60%	3.21	90	0.067	0.88	0.94

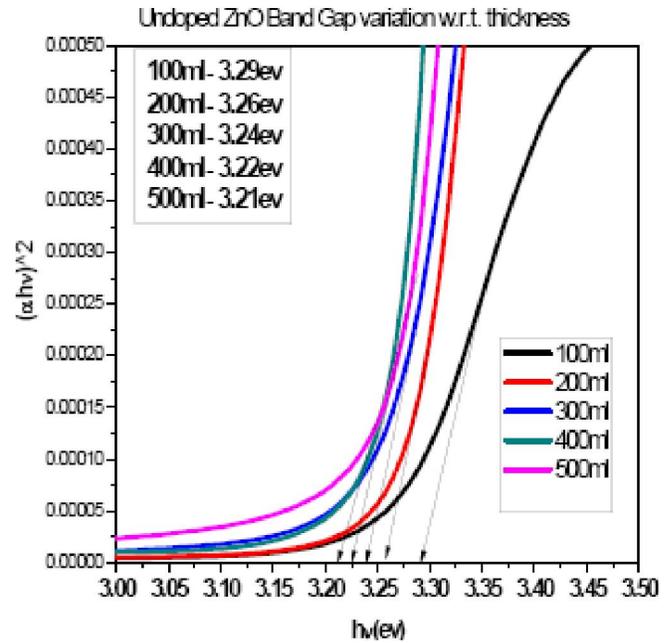
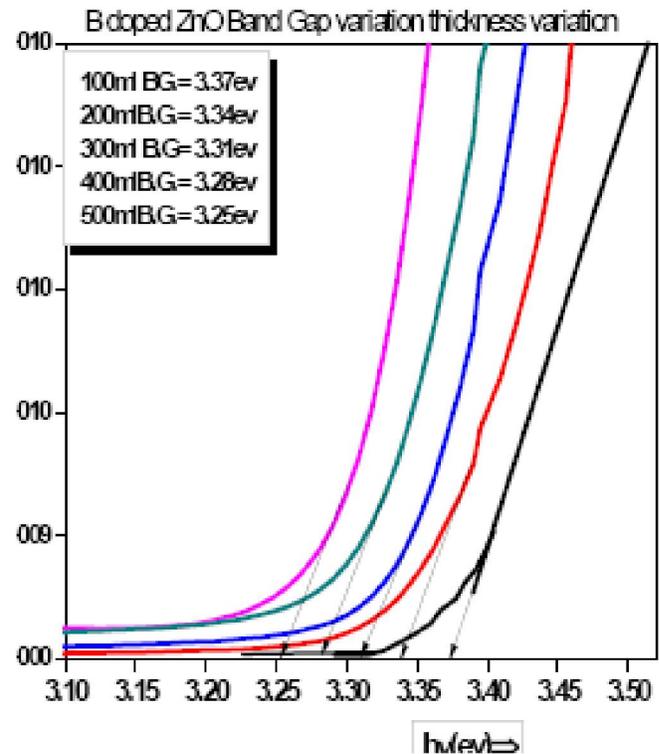
TABLE 3.2 : Optical & electrical characterization B: ZnO

Solution quantity	Avg. trans. (%)	B.G.(ev)	Sheet Res. (K.Ω)/cm ²	Fig.of merit 10 ⁻⁵ (Ω) ⁻²	Activation energy (ev)	
					E1ev 300-400 ⁰ K	E2ev 400-500 ⁰ K
100ml	90%	3.37	11.459	3.16	0.992365	1.24252
200ml	85%	3.34	5.26	3.74	0.74131	0.91609
300ml	80%	3.31	3.169	3.26	0.63126	0.90438
400ml	75%	3.28	3.38	25.4	0.5953	0.87339
500ml	65%	3.25	1.36	48.6	0.404082	0.57315

transmittance of both films decreases with increasing thickness of thin film. From TABLE [3.1] and [3.2], it is observed that B doped films have higher optical transmittance than undoped thin films. The optical properties of films are influenced by both doping as well as thickness of thin film. In order to better investigate the influence of thickness on the absorption of the ZnO films, the recorded transmission spectra were employed for the determination of the optical energy gap E_g . Assuming a direct transition between the edges of the valence and the conduction band, the variation of the absorption coefficient α with the photon energy $h\nu$ can be given by the following equation:

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (4)$$

Tauc's plot^[22] of $(\alpha h\nu)^2$ as a function of the energy of incident radiation has been shown in Figure [5] & [6]. The energy band gap is obtained from intercept of the extrapolated linear part of the curve with the energy axis and the band gap is observed to vary in between 3.21eV to 3.29eV for undoped ZnO thin films and 3.25eV to 3.37eV for B:ZnO thin films. Thus doping of

**Figure 5 : ZnO Band Gap****Figure 6 : B: ZnO Band Gap**

Boron causes blue shift in band gap. This may be due to deteriorated crystallinity affected by doping.

These observed values of optical band gap are in good agreement with the previous reports by others^[23,24].

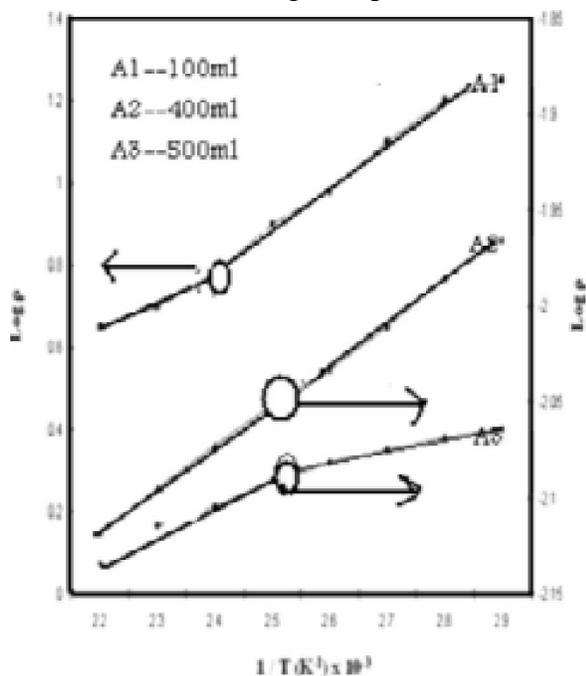
Electrical characteristics

Thickness varied electrical resistivity measurement

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was carried out by two-point probe method within temperature range 300–500K for both undoped and Boron doped thin films. The room temperature electrical resistivity of as-deposited B:ZnO film for thickness 102nm is of the order of $10^{-1} \Omega\text{-cm}$ which decreased to $10^{-2} \Omega\text{-cm}$ with increasing thickness to 486nm. The decrease in resistance with increase in temperature indicates the normal semiconductor behavior. On the other hand, the room temperature resistivity of ZnO film was decreased from $>1\text{M}\Omega\text{-cm}$ to $100\text{K}\Omega\text{-cm}$ with increase in film thickness from 75nm to 420nm. Thus the room temperature resistivity of sprayed ZnO films falling almost linearly with increasing thickness, in which the decreasing trend can be attributed to the inverse linear dependence of film resistivity increase on grain size. The growth in grains with film thickness leads to reductions in grain boundary scattering due to charge carriers, thus decreases the resistivity for the obtained films and eventually reduces the film resistivity.

Arrhenius plot of $\log(\rho)$ against $1/T$ (Figure 7, 8) indicates the semiconducting nature of thin films. For both films two distinct conduction regions are observed at low (300–400K) and high temperature (400–500K)



Variation of resistivity w.r.t. temp. for undoped :

Figure 7 : Arrhenius Plot ZnO

region which indicates more than one conduction mechanism. From Figure [7, 8], it is clear that the value

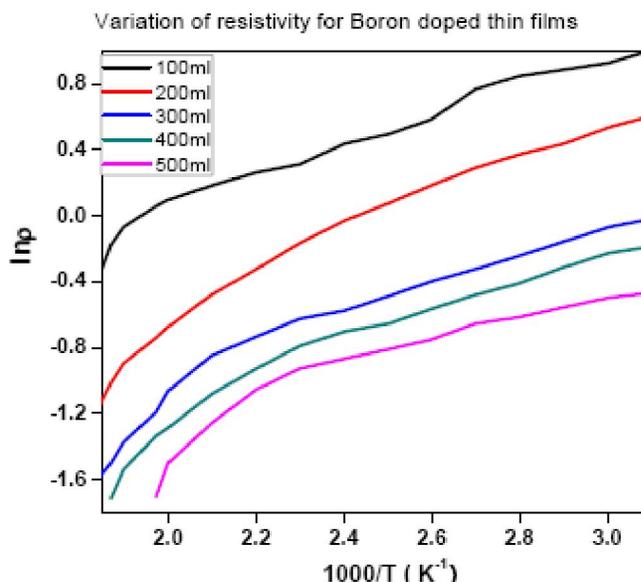


Figure 8 : Arrhenius Plot B: ZnO

of electrical resistivity decreases with increasing thickness. It may be due to improvement in crystallite size with increasing thickness of thin film. The growth in grains with film thickness leads to reductions in grain boundary scattering due to charge carriers, thus decreases the resistivity for the obtained films and eventually reduces the film resistivity. The activation energy was obtained using the relation,

$$\rho = \rho_0 \exp(-E_a/kT) \quad (5)$$

where ρ is the resistivity at any temperature, ρ_0 is the resistivity at absolute zero temp. E_a is activation energy 'k' is Boltzmann constant and T absolute temperature. The resistivity studies show that all the films exhibit two activation energies at different temperature regions. These activation energies vary with film thickness and are listed in TABLE [3.1 & 3.2]. It is observed that activation energies for undoped films have high values as compared to B:ZnO thin films. The variation of activation energy with solution quantity for undoped and Boron doped films is shown in Figure 9. The presence of defects levels due to small impurities in Zn source (99.95% pure) are expected to remain same in all the prepared films irrespective of B dopant concentration. However, the possibility of small influence of impurities available in B source on the activation energy of B doped ZnO film may not be ruled out. Considering the accuracy of the data (<7%), a linear decrease in the activation energy with an increase in B dopant content was observed, and is mainly attributed

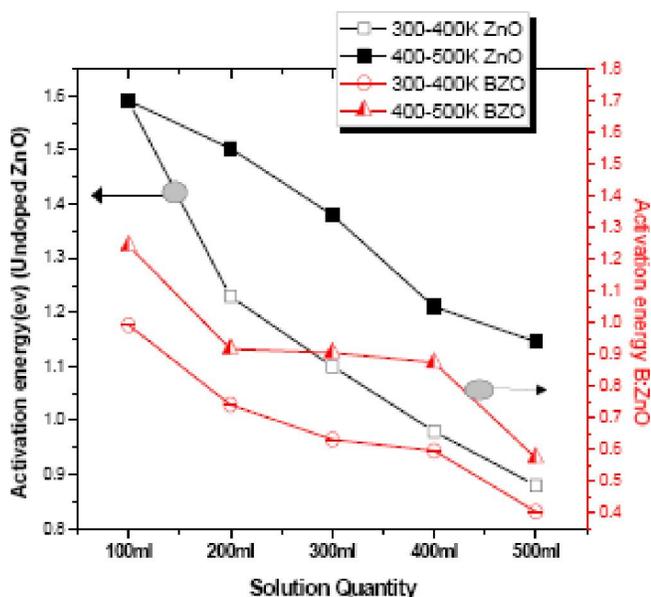


Figure 9 : Activation Energy

to the incorporation of B at Zn lattice site. The value of activation energy was found to decrease linearly with increase in B doping.

CONCLUSION

Both undoped & Boron doped ZnO films are synthesized by advanced spray pyrolysis technique deposited at low substrate temperature. All the films exhibit hexagonal wurtzite structure with (002) preferred orientation of grain growth. Boron doping deteriorates the crystallinity & strongly influences the optical properties of the ZnO thin films. The observed increase in optical band gap due to Boron doping compared to undoped films can be due to the effect of the Burstein Moss (BM) effect. Increased thickness and doping of Boron causes to increase the electrical conductivity.

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