"Synthesis and properties of Boron doped ZnO thin films by spray CVD technique at low substrate temperature"

Sunanda C. Yadav*
Thin film Physics laboratory, Department of Electronics, Shivaji University,
Kolhapur-416004, Maharashtra, India,
scyadav12@gmail.com

Mahadev D. Uplane,
Thin film Physics laboratory, Department of Electronics, Shivaji University,
Kolhapur-416004, Maharashtra, India

Abstract:-

Intrinsic and nanocrystalline properties of Boron doped ZnO thin films were synthesized with a newly designed spray CVD technique from non-aqueous solution of Zinc acetate [$Zn(CH_3COOH)_2$] as a precursor solution and Boric Acid as a doping solution. The major benefits of this technique are precise stoichiometry and its ability to deposit vapors on a large surface area with a high uniformity of thickness. The commercialization potential is enhanced by the low deposition temperature. In view for providing thin films as a Transparent Conducting Oxide (TCO) for commercial application, the effect of dopant concentration from 0.2 at% to 1 at% in steps of 0.2 has been studied. The crystalline properties of these films have been investigated by X- ray diffraction (XRD) technique. The results reveal hexagonal wurtzite structure indicating preferential orientation along c-axis. Debye –Scherrer calculation indicate deteriorated crystallinity induced by Boron doping. The results are in well agreement with surface morphology of film analyzed with Field Emission Scanning Micrographs and topography of films characterized with AFM. Moreover, the Boron doping enhances optoelectronic properties. 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 resulted with reduced particle size. Nevertheless, refractive index and absorption edge of the ZnO films are similar to that of single crystal ZnO. The significant effect indicating enhanced electrical conductivity of the ZnO film is observed for the optimized B dopant concentration (0.8 at %). The films obtained at 200°C show the highest carrier concentration $\approx 10^{20}cm^{-3}$ with lowest resistivity of $0.39x10^{-3}$ Ωcm. From the temperature dependence of conductivity measurements, the activation energy of the films was also calculated.

Keywords: Spray CVD technique, nanocrystalline, Transparent Conducting Oxide, AFM

1. Introduction

Transparent conductive oxide (TCO) thin films and coatings are the foundation of science and technology. Currently research on TCO has triggered by different applications in the number of electro-optical devices such as liquid crystal flat panel display, transparent electrodes, solar cells, light emitting diodes, transparent thin-film transistors (TTFTs) , heating element in air craft, car windows for defogging and de-icing , gas sensors, window layer, optoelectronic devices etc. Different metal oxide semiconductors such as In_2O_3, SnO_2, ZnO, and TiO_2 has been extensively studied and widely applied to fabricate TCO thin films. Among these a major driving force of research in ZnO material is its comparable photoelectric properties, wide band gap semiconductor for light emitting devices, relatively low cost, non toxicity and abundance in nature. However ZnO thin films exhibit moderate resistivity. It markedly depends on oxygen vacancies as well as zinc interstitial defects. The electrical properties of these films can be easily tuned providing accountable effect of electrical conductivity by incorporation with appropriate impurities of Group III elements such as Indium, Gallium, Boron, Aluminium etc. The efficiency of dopant depends on its electric negativity and ionic radius. However, literature survey reveals few reports with Boron dopant. It can be a promising cationic doping candidate owing to its ionic radii similar to Zn^{2+} ions.

Numerous methods has been employed to grow B doped ZnO thin films. Pawar *et al* [2005], have applied spray pyrolysis method, GAO Li *et al* [2011] have applied rf magnetron sputtering method, Hikavyy A. *et al*[2007] applied atomic layer deposition for deposition, X.L. Chen *et al* [2007], applied metal organic chemical vapor deposition technique, Miyata Toshihiro *et al* [2007] have applied vacuum arc plasma evaporation. Our approach was to obtain transparent, conductive and intentionally doped Zinc oxide thin films.

We have used the spray CVD technique to explore the effect of B dopants (0.2at% to 1 at% in steps of 0.2) into ZnO matrix. It is a versatile technique enabling deposition of large-area, uniform films, at very low substrate temperature and has found industrial applications. In the routine spray pyrolysis method the direct droplet deposition at the substrate takes place. These droplets wet the substrate and do not have surface uniformity. But in spray CVD method aerosol assisted chemical vapor deposition at the substrate takes place. It yields extremely high quality, uniform thin films. This paper investigates the dopant concentration of Boron, at low substrate temperature of 473 K produce both the high carrier concentration as well as maximum transparency. The films appear better crystallinity with preferred (002) orientation, exhibits maximum visible transparency (>90%) with higher carrier concentration ($>10^{20}cm^{-3}$). These results indicate that such B: ZnO thin films synthesized by novel spray CVD technique have fewer defects with maximum ordered crystallites showing complete decomposition of droplets and can be tailored at low substrate temperature which can be applied for cheaper large area solar cells.

2. Experimental techniques

Boron doped zinc oxide thin films were deposited by using spray CVD technique. A 0.075M solution of Zinc acetate dihydrate [Zn $(CH_3COO)_2$, $2H_2O$] in methanol was used as the main solution. For doping of Boron, non aqueous solution of boric acid was added to starting solution. The doping concentration range was varied from 0.2at% to 1 at% in steps of 0.2at%. Compressed air having constant flow rate of 10 lpm was used as a carrier gas. During deposition the solution flow rate of 6ml/min was kept constant by keeping the spray nozzle to substrate distance of 38cm. 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. It is noteworthy that each film was deposited for 3times and the obtained results confirmed that the films are reproducible.

The films prepared by the aforementioned technique were characterized for their properties by several characterization techniques. The crystallinity of the films was investigated by using a Bruker AXS X-ray diffractometer. The film surface morphology was studied with Field emission scanning electron micrographs (FESEM) at 50,000×magnification. Optical transmittance was measured using a double-beam spectrophotometer (Shimadzu UV-1800model), with an uncoated substrate in the reference path of the beam. The electrical properties of the B: ZnO films were determined by van der Pauw Hall effect set up supplied by Scientific Equipments, Rookie, India. Colloidal silver paste was used for ohmic contacts. Photoluminescence spectra of the samples were recorded with a spectrofluorimeter JASCO, model –F.P.-750, Japan using a 260nm line of an ultraviolet lamp as an excitation source. The three dimensional morphology of the growth was examined by using atomic force microscopy (AFM), Nanoscope instruments, USA in contact mode, with V shape silicon nitride cantilever of length 100μm and spring constant 0.58N/m. The thickness of the film was measured using a surface profilometer (AMBIOS-XP-1) with an accuracy of 20nm.

3. Result & Discussion

During deposition atomized droplets arrive in reaction chamber where thermal decomposition of the initial ingredients takes place. Small particles of the final product are pushed upward by air currents in reaction chamber and reach the preheated substrates. It offers initial nucleation centers for growth of thin film and provides average kinetic energy for even distribution of the deposits. Finally thin transparent layer of BZO thin film is formed on the glass substrate. The first stage of optimization of the growth of ZnO thin films was to study the dependence of their crystallinity as a function of doping concentration.

3.1. X-ray Diffraction Studies

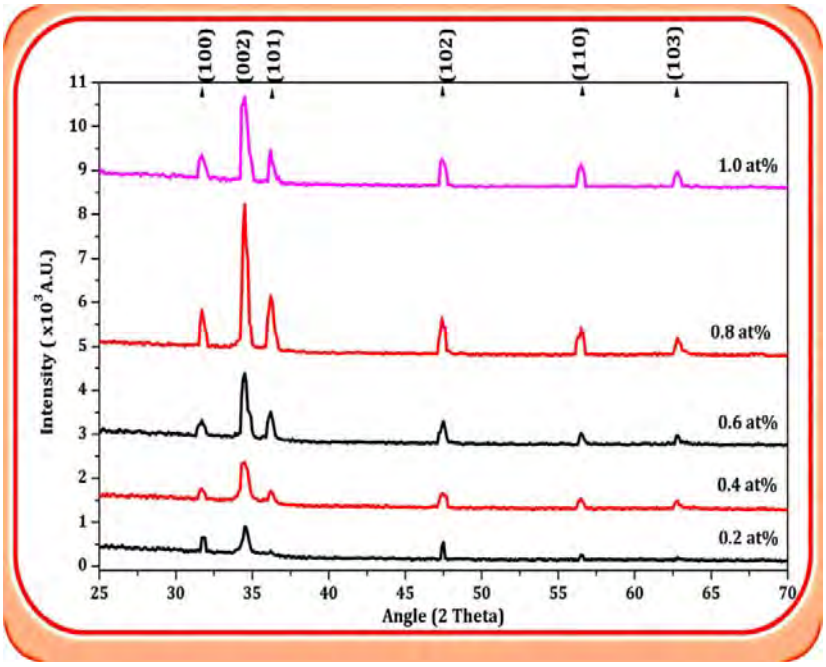

Fig.1 XRD Spectra of varying Boron doping concentration

In the present study, the microstructure of spray-CVD deposited Boron doped ZnO films has been analyzed as a function of the doping content. Micro-structural aspects contributing to the films state of structural parameters have been considered. Fig. 1 shows the key role played by different doping concentration of boron in the structural growth of ZnO thin films. It shows that the structural properties of the ZnO films strongly depend on doping concentration. For both ZnO and ZnO: B films, the dominant diffraction peak is the (002) peak at around 34.4°, confirming the strong (002) texture of these films. The dominant peak arises from diffraction of ZnO planes of grains oriented with c-axes perpendicular to the substrate. Although it has been shown that the (002) direction in ZnO, obtained in equilibrium growth conditions, has the lowest surface energy. Similar texturing of the films has also been observed by Pawar B.N. et al [2005], & Lokhande B. J. et al [2001]. Three well-defined peaks, identified as the (100), (002), and (101) diffraction planes of ZnO, are clearly observed in both diagrams, along with less intense peaks (102), (110), (103), (200), (112) indicating the polycrystalline wurzite structure of ZnO. The d values of thin films were in good agreement with those reported in the PDF for ZnO (JCPDS card file no:. 80-0075, a = 3:24982and c = 5.20661 Å).

3.2 Surface Morphology

The morphologies of ZnO nanocrystals exhibited striking dependence on the concentration of dopant ions with transition of shapes into cluster of islands, nanospheres, and finally into petal shaped morphology.

In the synthesis of ZnO nanocrystals, introduction of B dopants leads to dramatic shape evolution in addition to the compositional variation of the resulting nanocrystals. The mechanism related to the shape evolution of the B doped ZnO nanocrystals was explored. With increasing boron content the shapes of the grains deteriorate and the size of these grains decreases and also some porosity is observable on the surface. At higher doping level, smaller average grain size produces a surface roughness reduction and, as a consequence, less-textured films with lower light-scattering properties. However, the films deposited for 0.8 at% Boron doping concentration shows nanospherical uniform grains which may cause to enhance the c-axis orientation of crystallites observed in fig.1.

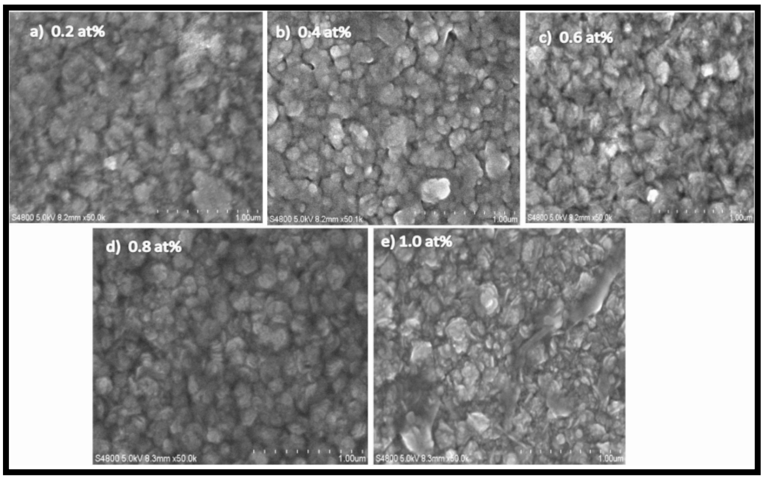

Fig.2 Surface Morphology for varying Boron doping concentration

3.3 Surface Topography

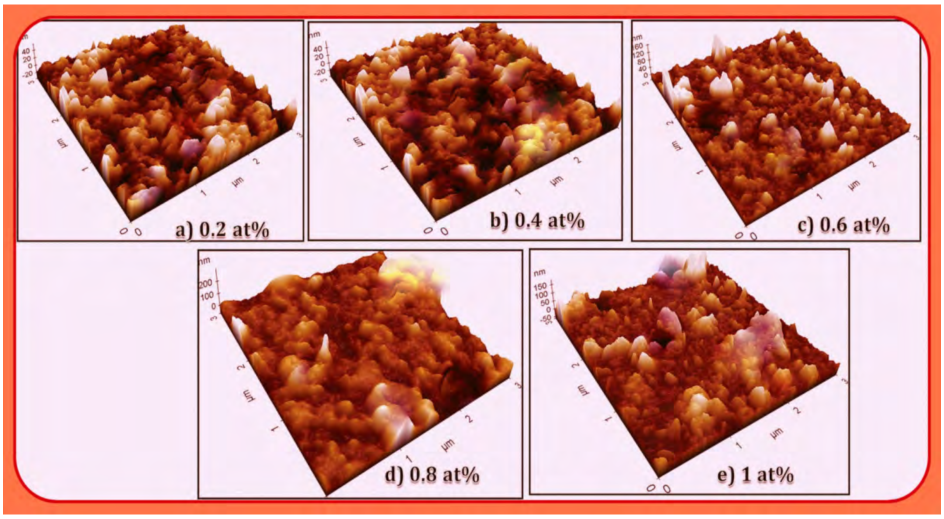

Fig.3 Surface Topography for varying Boron doping concentration

From the images it is seen that all the film surfaces are well covered with the uniformly distributed spherical grains of varying sizes. It is evidently seen that addition of Boron changes the topography of films from clusters into well defined spherical grains which are correlated with FESEM morphology. As seen from figure 3, the 3D micrographs revealed that Boron doping reduces roughness of thin film indicating very smooth surface for 0.8at%. It is observed that increase in doping concentration causes to increase in thickness of thin films, this may be due to smaller ionic radius of Boron than Zinc which causes to increase ionic bonding between Boron and Oxygen as compared to the ionic bonding between Zinc and Oxygen. This strong bonding between Boron and Oxygen reduces the rate of evaporation resulting in to increase in thickness of thin film.

3.4 Electrical Resistivity

Figure 4 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 behaviour. 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.

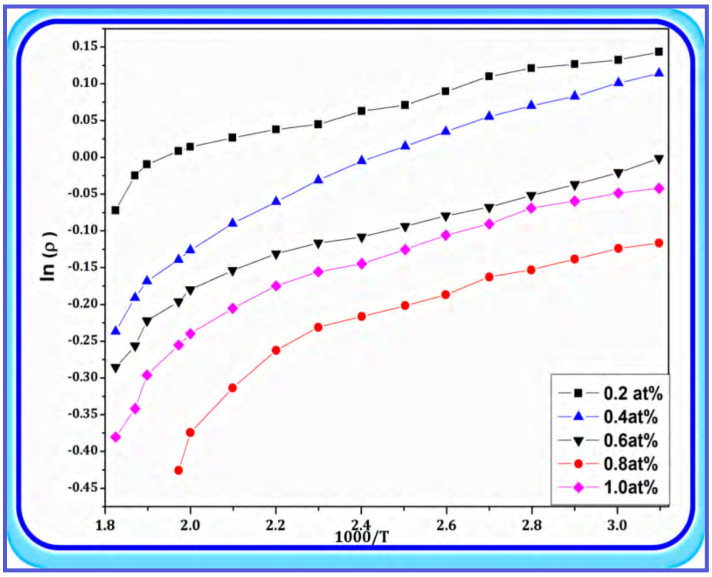

Fig.4 Arrhenius Plot for varying Boron doping concentration

It shows that the activation energy in the low temperature region is always less than the energy in the high temperature region this is because material transfers from semiconducting behaviour to metallic behaviour with increase in temperature. In the low temperature region of conduction, the decrease in resistivity may be due to the increase in mobility of charge carriers, hence small thermal energies are quiet sufficient to activate these charge carriers to take part in conduction process. In high temperature region, the conduction is attributed to the intrinsic defects caused by the thermal fluctuations. Thus the high value of activation energy is mainly determined by the intrinsic defects and hence is called as intrinsic conduction.

Table 1 Activation Energy

Doping concentration	**Low temp region 60^0C-150^0C**	**High temp region 150^0C-300^0C**
0.2at%	0.035eV	0.18eV
0.4 at%	0.065 eV	0.66eV
0.6 at%	0.039eV	0.35 eV
0.8at%	0.093eV	0.17eV
1 at%	0.022 eV	0.28 eV

3.5 Optical Properties

The optical transmission of the Boron doped ZnO thin films synthesized by spray CVD system on corning glass substrates were measured by using UV spectrophotometer in the wavelength range 360nm to 1000nm and is as shown in figure 4.10. It shows variation of spectral transmittance with wavelength for concentration variation in the range 0 at% and 0.4 to 0.8 at% (in steps of 0.2 at %).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. As observed for undoped ZnO thin films, the transmittance curves with variation of Boron doped thin films also show interference fringe pattern between the wave fronts generated at the two interfaces (air and substrate). The pattern defines the 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.

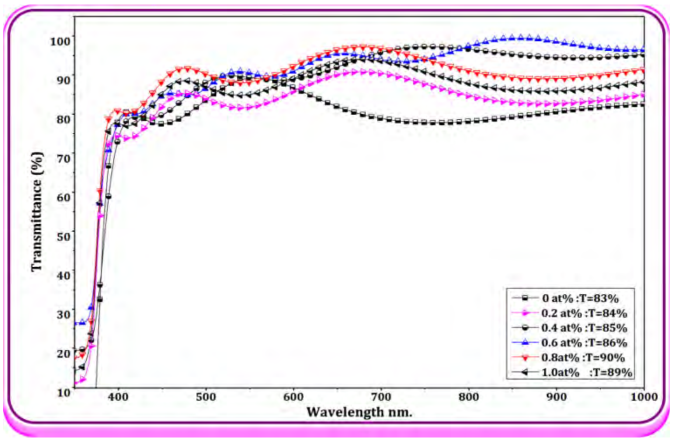

Fig.5 Optical Transmittance of B doped ZnO thin films

4. Conclusion

Highly transparent, conductive Boron doped ZnO thin films have been successfully deposited by spray CVD technique. The effect of variation of Boron doping concentration on the structural, electrical & optical properties has been studied. The structural analysis shows that the films are polycrystalline with preferential orientation along [002] direction. For 0.8at% optimized Boron doping concentration the films exhibit maximum conductivity showing optical transmittance ≈90%. These films exhibit best values comparable with other depositions. Hence the novel spray CVD technique is more sophisticated technique for deposition of Boron doped ZnO thin films at low substrate temperature.

Acknowledgement

One of the authors Mrs. S. C. Yadav, is grateful to Prof. B. B. Kale Sir CEMET, Pune for providing the facility of FESEM.

5. References

[1] Pawar B.N., Jadkar S.R., Takwale M.G., (2005), Deposition and characterization of transparent and conductive sprayed ZnO:B thin films, J. of Physics and Chemistry of Solids 66, 1779–1782

[2] Gao Li , Zhang Yan, Zhang Jian-Min, Xu Ke-Wei, (2010), Boron doped ZnO thin films fabricated by RF-magnetron sputtering, Applied Surface Science xxx

[3] Hikavyy A., Clauws P., Vanbesien K., De Visschere , Williams O. A., Daenen M., Haenen K., Butler J.E., Feygelson T. (2007), Diamond & Related Materials16, 983 – 986

[4] Chen X.L., Xu B.H., Xue J.M., Zhao Y., Wei C.C., Sun J., Wang Y., Zhang X.D., Geng X.H., (2007), Boron-doped zinc oxide thin films for large-area solar cells grown by metal organic chemical vapor deposition, Thin Solid Films 515, 3753 – 3759

[5] Miyata Toshihiro, Honma Yasunori, and Minami Tadatsugu,[2007], Preparation of transparent conducting B-doped ZnO films by vacuum arc plasma evaporation , J. Vac. Sci. Technol. A, Vol. 25, No4

[6] Pawar B.N., Jadkar S.R., Takwale M.G., (2005), Deposition and characterization of transparent and conductive sprayed ZnO:B thin films J. of Physics and Chemistry of Solids 66, 1779–1782

[7] Lokhande B.J., Patil P.S. , Uplane M.D. (2001), Studies on structural, optical and electrical properties of boron doped zinc oxide films prepared by spray pyrolysis technique, Physica B 302–303, 59–63