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Properties of ZnO:Bi thin films prepared by spray pyrolysis technique

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ABSTRACT

Undoped and Bi doped zinc oxide thin films were deposited on glass substrate at 450 °C using spray pyrolysis technique. The X-ray diffraction studies shows that Bi doped ZnO films are polycrystalline hexagonal structure with a preferred orientation along (1 0 1) direction. Crystallites size of the films decreases with increasing doping concentration. Scanning electron microscope image shows change in the surface morphology. The composition of Zn, O and Bi elements in the undoped and Bi doped ZnO films were investigated by X-ray photoelectron spectroscopy. Bi doped ZnO thin films show a transparency nearly 75% in the visible region. The optical band gap of ZnO thin films reduces from 3.25 eV to 3.12 eV with an increase in Bi concentration from 0 to 5 at.% respectively. Electrical conductivity of ZnO thin films increased from 0.156 to 6.02 S/cm with increasing Bi dopant concentration from 0% to 5% respectively.

1. Introduction

Zinc oxide (ZnO) belongs to II–VI compound semiconductor with properties of wide band gap of 3.37 eV, high bond strength with high exciton energy 60 meV and high optical gain at room temperature [1]. Due these properties ZnO have many applications in optoelectronic device such as flat panel displays [2] and light emitting diodes [3]. ZnO can be used as transparent conducting oxide (TCO) [4]. The most commonly used TCO's are indium doped tin oxide (ITO) and tin oxide (SnO_2). However, the optical and electrical properties of undoped ZnO donot reach the requirements of high performance semiconductor devices [5]. In order to enhance these properties ZnO should be doped with various dopants. Doping of ZnO with Al, In and Ga were widely investigated by various group of researchers [6–8] and it resulted in n-type conductivity. In the present study bismuth has been selected as the doping element. Since there were few reports on Bi doped ZnO thin films compared with Al, Ga, In doped ZnO thin films. Jiang et al. [9] studied the effect of argon pressure on the structural, optical, and electrical properties of the Bi doped films using rf magnetron sputtering. Ogawa et al. [10], reported the superconducting properties of ZnO-doped (Bi, Pb)-2223 thick film on Ni and NiO substrates prepared by spray deposition technique and Mista et al. [11] studied the varistor performance of nanocrystalline Zn–Bi–O thin films prepared by reactive RF magnetron sputtering at room temperature. The effects of Bi doping on the structural, compositional, optical and electrical properties of spray deposited ZnO films has been presented in the paper.

Different methods have been employed to deposit the doped ZnO thin films such as pulsed laser deposition [12], sputtering [13], physical vapour deposition [14], sol–gel method [15] and spray pyrolysis method [16]. Among these methods spray pyrolysis is simple, inexpensive and useful for large area surface coating applications.

2. Experimental details

The bismuth doped zinc oxide thin films were deposited onto glass substrate using a starting solution of 0.05 M concentrations of zinc acetate anhydrous [$Zn(CH_3COO)_2$] in methanol [CH_3OH]. Bismuth nitrate [$Bi(NO_3)_2$] is used as a source of dopant. The dopant concentration is varied from 0 to 5 at.% by changing the molar ratio in the spray solution. This solution was sprayed onto the heated glass substrate by means of spray nozzle at the constant pressure of 0.2 Torr. The substrate temperature is maintained at 450 ± 5 °C to deposit the undoped and doped ZnO films. Air is used as carrier gas. The separation between the substrate and nozzle was optimized to get the uniform film deposition. Both undoped and Bi doped films were annealed at 450 °C for 4 h in air.

The thickness of deposited films were maintained at 600 nm for the present study. The structural characterization of the film was carried out using X-ray diffractometer (XRD), with Cu kα radiation of wavelength $\lambda = 1.5418$ Å. The influence of Bi doping on the structure of ZnO thin films was investigated. Scherrer's method was used to determine the average size of crystallites from the broadening of diffraction peaks. Scanning electron microscope (SEM) has been used to record the surface micrographs of Bi doped ZnO thin films. The compositional analysis of undoped and Bi doped ZnO films were done using X-ray photoelectron spectroscopy (XPS). The optical measurements of undoped and Bi doped ZnO thin films were carried out using UV–Visible spectrophotometer in the wavelength range of

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300–800 nm at room temperature. The electrical characteristics of the films were studied using Keithley source meter and multimeter. The Hall measurements of undoped and Bi doped ZnO thin films were made at room temperature by using Van der Pauw method in a magnetic field strength of 0.5 T.

3. Results and discussions

3.1. Structural characterization

The XRD datas were used to study the structural properties of undoped and Bi doped ZnO films. Fig. 1 shows the XRD pattern of undoped and Bi doped ZnO thin films deposited at 450 °C. It is observed that all the films exhibits polycrystalline hexagonal wurtzite structure indexed according to the JCPDS 36-1451. There is no peak corresponding to Bi or related phases found in the diffraction pattern. It is seen from the XRD pattern that doping of Bi alters the orientation of the crystallites. The XRD pattern of undoped ZnO exhibits a preferential orientation along (002), whereas Bi doped films show reduced peak intensity along (002) direction and slightly increased peak intensity along (101) direction. This indicates that loss of preferential orientation of the films with Bi doping. Lee et al. [7] reported the change in the preferential orientation of In doped ZnO films prepared by pyrosol method. The average grain size (D) of deposited thin films were calculated from the X-ray diffraction pattern using Scherrer's formula [17],

$$D_{hkl} = 0.9\lambda/\beta\cos\theta \quad (1)$$

where λ is wavelength, β is full width at half maximum and θ is Bragg's angle. The calculations made on (002) diffraction peaks for the determination of crystallites size of the undoped and Bi doped ZnO films. The calculated value of grain size was shown in the Table 1. It is noted that crystallite size slightly decreased from 15.35 nm to 10.66 nm as the concentration of Bi increased from 0 to 5 at.%. This may be due to the presence of disorder in the ZnO lattice created by incorporation of Bi ions. The nucleation steps may change during film growth, the reduction in the nucleation centre may occur in the presence of Bi ions, this reduces the grain size. Acharya et al. [18] and srinivasan et al. [19] were also reported the decrease in grain size in the Cd and Mn doped ZnO films respectively. Even after the Bi doping, ZnO retains its hexagonal structure which confirms the stability of the film. The grain size changed and growth orientation of the ZnO films changed gradually from (002) to (101) with doping. Further lattice parameter a and c were unaffected by doping indicating no distortion in the lattice.

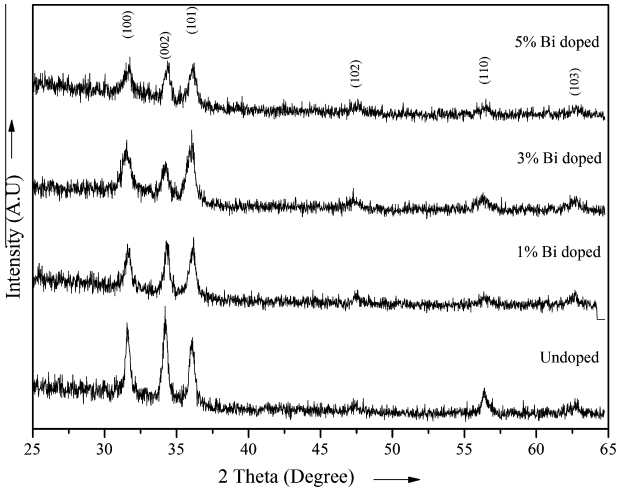

Fig. 1. XRD pattern of undoped and Bi doped ZnO thin films.

Table 1
XRD data of undoped and Bi doped ZnO thin films.

Bi (%)	Grain size (nm)	Lattice parameter (Å)	
		a	*c*
0	15.35	3.27	5.24
1	12.37	3.27	5.23
3	10.27	3.27	5.22
5	10.66	3.28	5.22

3.2. Morphological study

The scanning electron micrographs of undoped and Bi doped ZnO thin films were shown in the Fig. 2. It shows that the undoped films (a) have plane and uniform smooth surface. The surface morphology of the ZnO films shows marked changes on Bi doping. The granular morphology is seen in the each micrograph. The size of the granules increases as the dopant concentration increases from 1 at.% to 5 at.%.

3.3. Compositional analysis

The compositional analysis of undoped and Bi doped ZnO thin films was investigated using X-ray photoelectron spectroscopy (XPS). The XPS spectra of undoped and Bi doped ZnO thin films were shown in the Figs. 3 and 4. Fig. 3 shows the XPS spectra of (a) survey scan, (b) Zn2p, (c) O1s core level spectrum and (d) Zn3p core level spectrum of the undoped samples. The ZnO films shows two binding energy peaks at 1021.19 eV and 1044.63 eV corresponding to $Zn2p_{3/2}$ and $Zn2p_{1/2}$ core levels respectively. Fig. 3(c) shows the symmetric two O1s peak. The O1s peak for the undoped film is splitting into two sub spectral components. One is at 531.58 eV and other one is located at 530.12 eV.

The peak position on the low binding energy side of the O1s spectrum at 530.12 eV corresponds to O^{2-} ions on wurtzite structure of hexagonal Zn^{2+} ion array, surrounded by Zn atoms with their full complement of nearest neighbour O^{2-} ions [20]. The other component located at higher binding energy at 531.58 eV is arised either due to the loosely bound oxygen or due to the presence of hydrated oxides in the film. The atomic percentage of zinc and oxygen in the ZnO films were estimated and are found to be 36.46% and 63.54% respectively.

Fig. 4(c) shows the O1s XPS spectra of Bi doped ZnO films. There are two asymmetric O1s peaks are located at the binding energies 530.3 eV and 532 eV. The peak corresponding to the lower binding energy is due to Zn–O bond and the other peak located at the higher binding energy accords with the chemisorbed oxygen [21]. It is seen from the Fig. 4(c) that an O1s peak is moved slightly to the higher binding energy direction with Bi doping. This may be attributed to minor lattice distortion, which is not reflected in the lattice parameters.

The Fig. 4(d) shows Bi 4f core level XPS spectrum of 3% Bi doped samples shows two asymmetric peaks located at 158.7 eV and 163.9 eV calculated using Gaussian peak fitting. The peaks located at 163.9 eV and 158.7 eV can be assigned to Bi $4f_{5/2}$ and Bi $4f_{7/2}$ region, respectively. The peak located at 163.9 eV confirms the presence of Bi^{3+} in the ZnO lattice. [22]. The peak located at about 158.7 eV, which is attributed to the Bi–O bonding rather than Zn–Bi bonding in the Bi doped ZnO films. This is because no peaks located below 157.0 eV attributed to Zn–Bi bonding in the Bi doped ZnO films, the contents of Bi_O may be very small in the Bi doped ZnO films. Otherwise no peaks will be located at about 157 eV attributed to isolated Bi in Bi doped ZnO films [23]. The atomic percentage of zinc, bismuth and oxygen in the Bi doped ZnO films were estimated and are found to be 50.25%, 2.58% and 47.17% respectively.