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Influence of Zn doping on nanostructured Bi₂O₃ thin films

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Abstract: Nanostructured Zn doped Bi_2O_3 thin films was spray deposited on the glass substrate at the optimized temperature of 250°C. The structural studies confirm that the prepared film has -phase tetragonal structure with polycrystalline nature. The grain size was calculated to be around 30 to 40 nm. The annealing effect improves the crystallinity and reduces the defect present in the film. The nanoflake like morphology was seen in the surface studies, upon annealing an even nanoflake was seen on the film. From the optical studies the band gap of the film is found to be 3.25 eV and on annealing the band gap decreases to 2.8 eV. The transmittance varies between 30 % - 35% for as deposited film and 20% - 28% for annealed film. The electrical studies confirm the semiconducting nature of the film. The resistance of the annealed film is more than the resistance of the as deposited film. The influence of Zn incorporation and annealing effect on the electronic properties of Bi_2O_3 is discussed and reported.

Keywords: annealing, nanostructure, Bi₂O₃ thin film,optical studies.

Introduction

Bismuth oxides have the potential importance in the modern solid-state technology, due to its energy band gap, dielectric permittivity, photoconductivity and refractive index. Due to this properties Bi_2O_3 thin films are suitable for large application such as electrochemical supercapacitor[1], photocatalytic activity[2], optical coatings [3], fuel cells [4], oxygen sensors [5]etc., Bi_2O_3 has four crystalline phases which are monoclinic - Bi_2O_3 , tetragonal $-Bi_2O_3$, cubic γ - $Bi_2O_3(BCC)$ and cubic $-Bi_2O_3(FCC)$ [6].Different phases have its distinct electronic properties and crystal structure. The preparatory condition of the Bi_2O_3 plays an important role in the nanostructure depending on vapor phase or liquid phase technique. Some of the important vapor phase technique includes RF sputtering, laser ablation, chemical vapor deposition and thermal evaporation [7-9]. Likewise the liquid phase technique includes sol-gel, electrodeposition, chemical bath deposition and spray pyrolysis [10-13]. The electrical conductivity of Bi_2O_3 may be changed with the preparatorycondition; the energy band gap can also be fine-tuned from 2 to 3.9 eV[14]. The presence of the dopant plays a significant role in the band gap tuning.

From the survey, it was known that not much work has been reported in the spray deposited Bi_2O_3 thin films. In the present work, bismuth oxide thin films are prepared using spray pyrolysis incorporating the Zinc as impurity in order to fine tune the band gap and electrical conductivity. This report also compares the as deposited and annealed Zn doped Bi_2O_3 thin films. Structural, morphological, optical and electrical studies of as deposited and annealed Zn doped Bi_2O_3 thin films are discussed.

Experimental

Zn doped Bi_2O_3 thin films were deposited on the borosilicate glass substrate using spray pyrolysis method. The precursor solution was prepared with Bismuth (III) nitrate pentahydrate (Bi $(NO_3)_3.5H_2O$) dissolved in 25 ml of deionized water with a concentration of 0.1 M,then 25 ml solution of Zinc nitrate hexahydrate $(Zn(NO_3)_2, 6H_2O)$ is prepared with a concentration of 0.001M and both the solution were mixed to make up 50ml of precursor solution. 3 ml of acetic acid is added to the solution to maintain the acidity of the solution in order to dissolve the Bismuth (III) nitrate pentahydrate with constant stirring at room temperature. Prior to deposition the glass substrate were cleaned with deionized water and acetone. The substrate were cut to dimensions of 2.5 cm and then the colorless precursor solution was spray deposited on the preheated substrate kept at the temperature of 250°C.A constant pressure of 2kg/cm² is maintained with the spray rate of 3ml/minute during the spraying process. The as deposited Zn doped Bi₂O₃ thin film is seen in thick white in color and after annealing the color of the film changes to light yellow. In order to improve the crystallinity and to reduce the crystal imperfections, the as deposited thin film is annealed at a temperature of 250°C for one hour and slow cooled in the air atmosphere to attain room temperature. The structural studies of the Zn doped Bi₂O₃ thin film was studied using X-ray diffraction, (XPERT-PRO) diffractometer for X-ray diffraction. The surface morphology of the film was taken using Scanning electron micrograph model number (JEOL- 6701F). The optical studies were taken using UV/Visible double beam spectrophotometer (Perkin Elmer). Four probe method was used to study the electrical characteristics of thin film.



Figure 1. X- ray diffraction pattern of as deposited and annealed Zn doped Bi₂O₃ thin film

Results And Discussion

Structural Studies

The X-ray diffraction (XRD) patterns of as deposited and annealed Zn doped Bi_2O_3 thin film is shown in the Figure. 1. XRD peaks shows that the prepared Zn doped Bi_2O_3 are polycrystalline in nature with the tetragonal structure which are well matched with the JCPDS card number 78-1793. This infers the existence of

-phase structure of Bi_2O_3 the preferential orientation of the film is seen along the (2 0 1) plane. Examining the XRD pattern of the as deposited and annealed Zn doped Bi_2O_3 thin film, the as deposited film has only (2 0 1) plane with low intensity, when annealing the film, it improves its crystallinity and the preferential orientation is seen along (2 0 1) plane with other planes namely (0 0 2) and (1 0 2) planes. Annealing the films reduces the defects, removes hydroxide phase and improves the recrystallization process. To prepare the single phase Bi_2O_3 without the trace of oxide vacancies the films are annealed at 250°C for one hour, this leads to the recrystallization process. The grain size (D) of thin films is determined using the Scherrer's formula

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where D is the grain size, is full width half maximum of the peak, is the angle of diffraction and is the x-ray wavelength[15]. The grain size is calculated to be around 30 nm using the Scherrer's formula.

Surface Morphology

The surface morphology of the Zn doped Bi_2O_3 thin film was studied by the Field Emission Scanning Electron Micrograph. A nano flake like morphology with granules which is in the nanometric regime is seen in the thin film. Figure. 2 (a) and (b) shows the SEM image of as deposited and annealed Bi_2O_3 thin films. In the as deposited thin films nanoflakes with rough morphology are seen, upon annealing the nanoflakes with even morphology are observed. The grain size of the annealed thin films is found to be around 40 nm which is in close agreement with the calculated value of the grain size with Scherrer's formula.



Figure 2. Scanning Electron Micrograph image of as deposited and annealed Zn doped Bi₂O₃ thin film

Optical Studies

The band gap and the transparency is an important parameter in the optoelectronic devices. Analyzing the optical transmittance spectrum of Zn doped Bi_2O_3 thin film, the transmittance of 30% to 35% is observed for the as-deposited Zn doped Bi2O3 thin films, whereas when the film is annealed the transmittance found to decrease which is around 20% to 28%. The reason may be due to the annealing effect, the recrystallization process takes place which will orderly orient the atoms in the lattice which decreases the transmittance. The transmittance spectrum of as deposited and annealed Zn doped Bi_2O_3 thin film is 3.25 eV, when the film is annealed the band gap decreases to 2.8 eV. The annealing effect has the influence in band gap tuning. The optical band gap of the as deposited and annealed Zn doped Bi_2O_3 thin film is calculated from the forumla

$$(h)^2 = A(h - E_g)$$

where A and E_g are constant and optical gap respectively [16]. Figure 4 represents the energy gap of Zn doped Bi_2O_3 as deposited and annealed thin film. The band gap tuning is possible by the dopant and annealing effect.



Figure 3. Transmittance spectrum of as deposited and annealed Zn doped Bi₂O₃ thin film



Figure 4. Energy band gap of as deposited and annealed Zn doped Bi₂O₃ thin film



Figure 5. Resistance vs temperature characteristics of as deposited and annealed Zn doped Bi_2O_3 thin film

Electrical Studies

In the present work the electrical studies of Zn doped Bi_2O_3 thin film is carried out by linear four probe method. Figure 5 shows the resistance-temperature characteristics curve of Zn doped Bi_2O_3 thin films. From the resistance – temperature characteristic curve, with the increase in the temperature there is decrease in the resistance which infers the negative temperature coefficient characteristics of semiconductor [17]. Interestingly, the resistance of the annealed film is more than that of the as deposited film, due to the doping effect of Zn atom and the annealing effect which reduces the defect present in the film increases the resistance considerably, the presence of the defect in the film is one of the sources of charge carriers. The annealing effect and Zn incorporation in the Bi_2O_3 thin film will drastically affect the electrical properties.

Conclusion

The Zn doped Bi_2O_3 thin film was deposited on the glass substrate has -phase structure. The structural studies confirm the formation of -phase with polycrystalline nature. The preferential orientation of the film is seen along the (2 0 1) plane. The effect of annealing improves the crystallinity and reduces the crystal defects which is confirmed in the structural studies, there is an increase in the preferential orientation along (2 0 1) plane. A nanoflake like morphology is seen in the as deposited thin film, the annealing effect improves the crystallinity and an even morphology of nanoflakesis observed. The optical studies inferthat the transmittance of 30% - 35% is observed for as deposited film, when annealed the transmittance decreases to 20 % -28%. The energy gap of as deposited film is found to be 3.25 eV on annealing the band gap decreases to 2.8 eV. From the electrical studies the thin film shows a negative temperature coefficient which refers the semiconducting property of the film. The resistance of the annealed film seems to be more than that of the as deposited film due to annealing effect it improves crystallinity and reduces the defect present in the film which in turn increases its resistance. The incorporation of Zn impurity and annealing effect will fine-tune the energy gap, film resistance, morphology and orientation of the film. The electronic properties can be tuned by Zn incorporation and annealing which finds its potential importance in the engineering applications.

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