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Effect of Annealing on Spray Deposited Bi_2O_3 Thin Film

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ABSTRACT

Nanostructured thin films of Bismuth oxide (Bi_2O_3) was spray deposited on the glass substrate at an optimum temperature of 230°C. The structural properties confirm that the prepared thin films were polycrystalline in nature with β-phase tetragonal structure. The grain size was calculated to be around 10 nm. The crystallinity is improved after annealing. The morphological studies confirm the nanostructured thin film with nano flake like structure. From the optical studies the band gap is found to be 3.1 eV for as deposited Bi_2O_3 thin film, whereas 3.2 eV for annealed Bi_2O_3 film. The transmittance of as deposited film is 30% whereas for annealed film there was a decrease in the transmittance in the visible region. The electrical characteristics confirm that the prepared thin films were having semiconducting nature. The resistance – temperature characteristics of as deposited and annealed Bi_2O_3 were studied and reported. From the reported work by fine tuning the preparatory conditions, nanostructured Bi_2O_3 thin films can be synthesized which will well suit for engineering applications.

Keywords: spray deposition; annealing; Bi_2O_3 thin films; nanostructured

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INTRODUCTION

Bismuth Oxides (Bi_2O_3) has potential importance in modern solid state technology, the advantage of Bi_2O_3 thin film is it has a wide energy gap and the band gap can be tuned to optimize the required electronic property. Bi_2O_3 has high value of refractive index, dielectric permittivity and photoconductivity, and photoluminescence property [1]. Bi_2O_3 have a five different polymorphism which are represented as α, β, γ, δ, ω phases, among them α-phase is stable at low temperature and β-phase is stable at high temperature. δ -phase is metastable at high temperature. α- Bi_2O_3 has monoclinic structure, β- Bi_2O_3 has tetragonal structure, γ- Bi_2O_3 has cubic BCCstructure, δ- Bi_2O_3 has cubic FCC structure and ω- Bi_2O_3 has triclinic structure. Bi_2O_3 finds its potential applications in gas sensor [2], oxygen sensor [3], electro chromic material [4], nanoscale electronics, optoelectronics [5, 6], Bi_2O_3 is a good solid electrolyte due to its high oxygen ion conductivity, and it is also well suited for optical coatings and ceramic glass manufacturing. Bi_2O_3 can be prepared with different morphologies such as nanowire [7], quantum dot, quantum rod, nano belts, nano fibers [8] etc. Bi_2O_3 thin films are prepared by liquid phase technique such as chemical bath deposition [9], thermal evaporation [10], electro deposition [11], and spray pyrolysis [12]. Bi_2O_3 thin films can also be synthesized by vapour phase technique which includes RF sputtering [13], thermal evaporation [14], chemical vapour deposition [15] and pulsed laser deposition technique [16]. Since vapour phase techniques are expensive method, in order to obtain Bi_2O_3 film with controlled morphology, Bi_2O_3 film is synthesized by spray pyrolysis method. However, there is no much work reported with spray deposited Bi_2O_3 thin film. The motivation of this work is to prepare Bi_2O_3thin films with controlled morphology to tailor the structural, electrical and optical properties. In the present work, Bi_2O_3 thin film is deposited on the glass substrate and annealed to increase its crystallinity, the structural, morphological, optical and electrical studies were carried out to optimize the properties which maywell suit for the potential applications.

EXPERIMENTAL METHODS

Bi_2O_3 thin films were deposited on the borosilicate glass using spray pyrolysis method. The precursor solution is made with Bismuth (III) nitrate pentahydrate (Bi $(NO_3)_3.5H_2O$) with a purity of 98 % is dissolved in the 50 ml of deionized water at a concentration of 0.1 M. 3ml of nitric acid is added to the deionized water drop by drop to increase its acidic nature, in order to dissolve Bismuth (III) nitrate pentahydrate and by constant stirring at room temperature, the precursor solution was prepared. The glass substrates were cleaned before deposition and cut with the dimensions of 2.5 cm, then the colorless precursor solution is spray deposited on to the preheated substrate which is maintained at the temperature of 230^{o}C. The precursor solution is sprayed at a constant pressure of 2 kg/cm^2 with the spray rate of 3ml/minute. The as deposited Bi_2O_3 thin film is seen as white in colour. To improve the crystallinity. The as deposited film is annealed at a temperature of 230^{o}C for one hour and then slow cooled in the air to attain room temperature. The structural properties were studied using X-ray diffraction which employs (XPERT-PRO**)**. The morphological studies were taken using Scanning electron micrograph model number (JEOL- 6701F). The optical studies were carried out using UV/Visible spectrophotometer (PerkinElmer). The electrical studies were taken using four probe method to find the resistivity.

RESULTS AND DISCUSSION

Structural studies

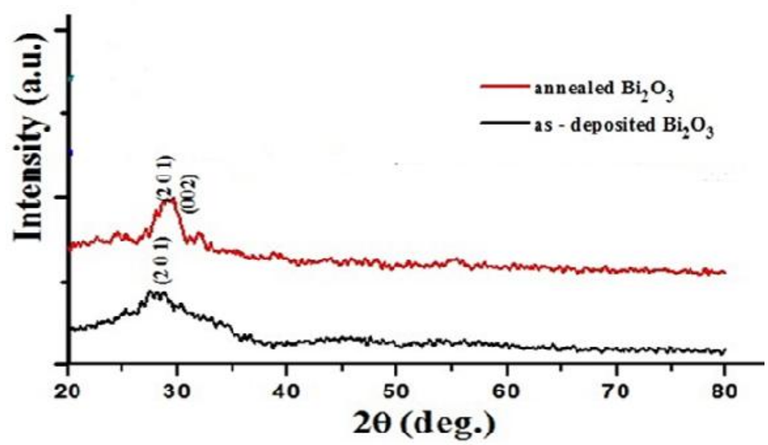
Structural studies were carried out to confirm the crystallinity in Bi_2O_3 thin film. X-ray diffractometer with CuK_α radiation (λ = 1.5418 Å) in the range of 20-80^o at a scan speed of 2^o per minute is used to scan the film. X-ray diffraction (XRD) patterns of as deposited and annealed Bi_2O_3 were given in the Fig.1,the diffraction peaks shows that the prepared Bi_2O_3 were polycrystalline in nature with tetragonal structure which agrees with the JCPDS card number. 78-1793. This refers to the β-phase structure of Bi_2O_3, the preferential orientation is seen along (2 0 1) plane. Analyzing the XRD pattern of as deposited and annealed Bi_2O_3 thin films the orientation of the plane is found to increase by which it is inferred the crystallinity is improved after annealing.

The grain size were determined using the Scherrer's formula

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

Where D is the grain size, β is full width half maximum of the peak, θ is the angle of diffraction and λ is the x-ray wavelength. From the Scherrer's formula the grain size is calculated to be around 30 nm [17].

Fig.1.XRD pattern of (i) as –deposited and (ii) annealed pure Bi_2O_3 thin film on glass substrate



Surface Morphology

The surface morphology was taken by the Field emission Scanning electron microscope, a nano flake like morphology is seen from the image which is in the nanometric range, and there is improvement in the grain is noticed for the annealed film. Fig. 2(a) and 2(b) shows the as deposited and annealed Bi_2O_3 thin film. The prepared film is in the nanometric regime. The grain size of the annealed film is found to be around 25 nm which is also in agreement with the calculated grain size with the structural studies.

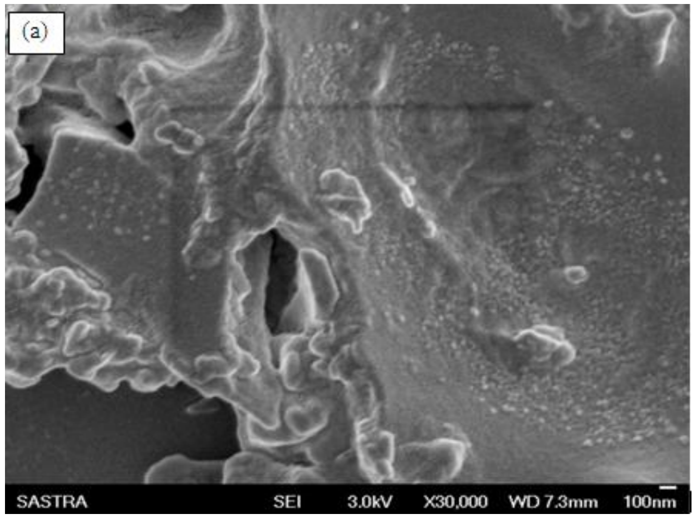


Fig.2. (a) SEM view of nanoflake shaped pure Bi_2O_3as-deposited thin film

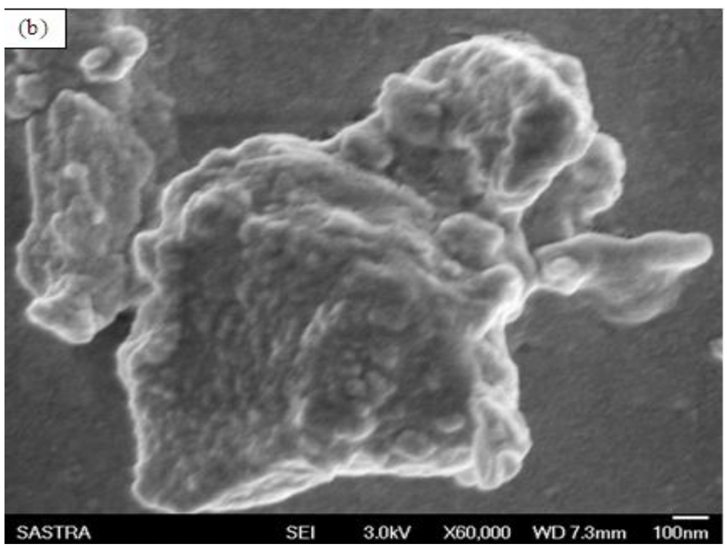


Fig.2.(b) SEM view of nanoflake shaped pure Bi_2O_3 annealed thin film

Optical Studies

The optical transparency and optical band gap is an important parameter for optoelectronic applications. The transmittance of the pure as deposited Bi_2O_3 film is around 30% - 35%. In contrast, when the film is annealed the transmittance decreases to around 25% - 30%. Due to the realignment of the atoms in the lattice the transmittance is found to decrease for the annealed Bi_2O_3 thin films. Fig. 3 shows the transmittance vs wavelength plot of as deposited and annealed Bi_2O_3 thin films. The optical energy gap of the as deposited Bi_2O_3 is seen to be 3.1 eV, whereas annealing effect of the film leads to the increase in the band gap, which is found to be around 3.2 eV. The effect of annealing leads to the band gap widening [18]. The band gap of the as deposited and annealed Bi_2O_3 thin film is calculated from the forumla as

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)$$

where A and E_g are constant and optical gap respectively.

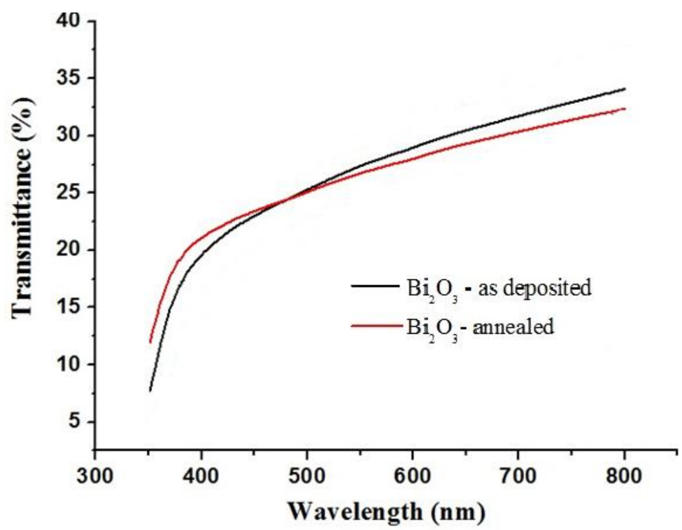
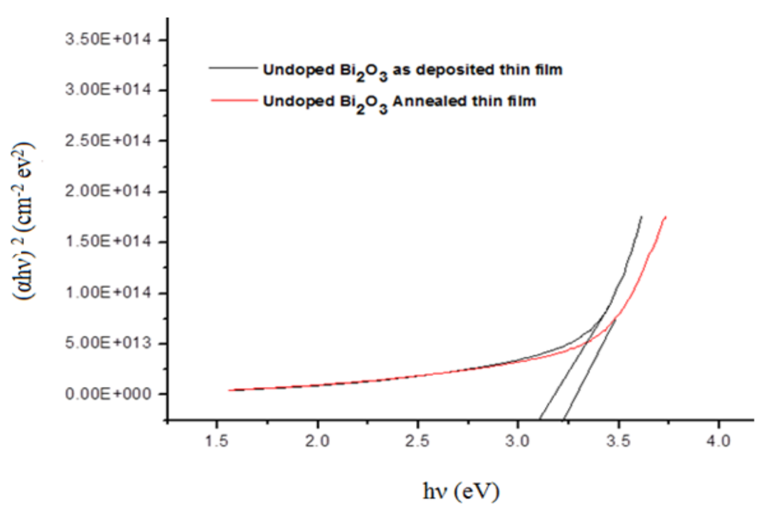


Fig.3. Transmittance spectrum of (i) as-deposited and (ii) annealed pure Bi_2O_3 thin film

Fig. 4 shows the energy gap diagram of as deposited and annealed Bi_2O_3 thin films. From the results it may be resolved that the band gap tuning is possible by annealing effect.

Fig.4.Plot of hυversus $(\alpha h\upsilon)^2$ for (i) as-deposited and (ii) annealed pure Bi_2O_3 thin film



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Electrical Studies

The electrical studies of the thin films were carried out using Four probe method. The resistance vs temperature characteristics curve is shown in the Fig. 5. The resistance-temperature characteristic curve confirms the semiconducting nature of the Bi_2O_3 films. The negative temperature coefficient is seen for the variation in the temperature. Looking at the R-T characteristics, initially the resistance is found to be low for as deposited Bi_2O_3 thin films than the annealed films, whereas for high temperature the resistance of as deposited films is more than the annealed film. Based on the electrical properties and optical properties the effect of annealing has the influence to increase or decrease the transparency and the electrical conductivity.The annealing effect will fine tune the electrical and optical properties which is suitable for the optoelectronic applications.

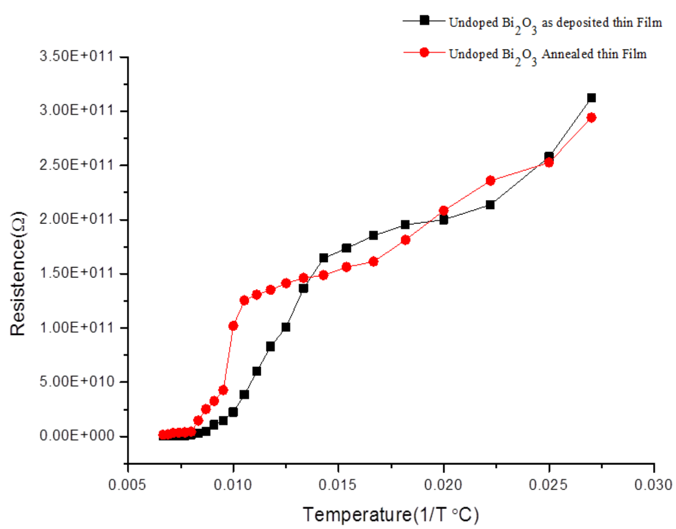

Fig.5. Variation of Resistance with temperature for (i) as-deposited and (ii) annealed pure Bi_2O_3 thin film

CONCLUSION

The β-phase structure of Bi_2O_3 is prepared with spray pyrolysis method. Structural studies confirms the formation of β-phase Bi_2O_3 thin film with polycrystalline structure, the preferential orientation is along the (2 0 1) plane. The annealing effect improves the crystallinity of the film. From the surface morphology of the films the nanoflake like structure is seen, improvement in the grain size is noticed with annealing. The nanoflakes are in the nanometric dimension. The optical transparency of the as deposited films is found to be around 35%, whereas for the annealed film it is in the order of 25%. The optical band gap for as deposited films is 3.1 eV and for annealed film it is 3.2 eV. The electrical studies confirms the semiconducting nature of the prepared film, initially for as deposited film at low temperature the resistance is found to be low compared to the annealed film, in contrast at high temperature the resistance of as deposited is more than the annealed film. The effect of annealing has the impact in improving the crystallinity, increasing or decreasing the resistance and transparency of Bi_2O_3 film which finds its potential importance in the optoelectronic devices and optical coatings.

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