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Thin Film Technology

Elixir Thin Film Tech. 101 (2016) 43922-43926

ISSN: 2229-712X

Annealing Effect on Structural, Optical and Electrical Properties of Bismuth Selenide Thin Films Using Chemical Bath Deposition Method

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ARTICLE INFO

Article history:

Received: 13 October 2016;

Received in revised form:

27 November 2016;

Accepted: 10 December 2016;

Keywords

Chemical bath deposition,

XRD,

Optical band.

ABSTRACT

Good featured glassy bismuth selenide (Bi_2Se_3) thin films were prepared from solutions having bismuth nitrate, triethanolamine and sodium selenosulphate at room temperature by chemical bath deposition technique. The crystalline structure, surface morphology, electrical and optical properties of these Bi_2Se_3 thin films were investigated as a function of annealing process. X-Ray diffraction studies resulted in Bi_2Se_3 thin films with amorphous structure at room temperature (RT) and growth in film was found by annealing with hexagonal crystal structure. A uniform sphere-like morphology was observed from scanning electron microscopy upon annealing. Optical absorption studies revealed that a direct band gap of 1.11 eV for as-deposited Bi_2Se_3 films and is drops to 1.02 eV by annealing in air at 200^0C for one hour. Moreover the absorption edge shifting toward longer wavelength associated with crystallinity development of annealed film. As-deposited, the thin films show resistivity of approximately 6kΩ/cm^2 decreases upon annealing. From temperature-resistance measurements Bi_2Se_3 thin films are distinctive semiconductor material upon annealing, with calculated activation energies of 0.18eV and 0.9eV at lower and higher temperature respectively. In photoconduction studies after annealing, the films display organized rise in the photocurrent with applied voltage than in the as-prepared films. This enrichment in conductivity results from crystallinity development along with partial loss of selenium. This may accelerate various promises for the usage of these films by chemical bath deposition method.

1. Introduction

Semiconducting thin film materials (sulfides, selenides and tellurides) performed a vital part in optoelectronics. Among bismuth selenide (A^VB^{VI} family) has extensive potential applications in IR photography, modern thermoelectric cooling modules, photo electrochemical cells and electro-thermal devices, Hall magnetometer and humidity sensors using Seeback and Peltier effects [1-6].

Due to narrow direct band gap (E_g = 0.16-0.35 eV) semiconducting property [7,8] and anisotropic layered structure, Bi_2Se_3 has fascinated uses in the field of optical recording systems and strain gauges [9]. The attractive industrial applications [10] also tempt to make and analyze the material by various deposition techniques [1, 11-17].

In this paper, we report the synthesis and characterization of Bi_2Se_3 thin films, by chemical bath deposition technique with annealing effect. The structural, optical, and electrical properties of these films are studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis absorption spectroscopy, photo conduction measurements and four probe method.

2. Experimental Details

2.1. Preparation of Bi_2Se_3 thin films

Bismuth selenide (Bi_2Se_3) thin films were deposited onto highly cleaned glass substrates by chemical bath deposition method. Bismuth nitrate pentahydrate and selenium powder was used as precursor materials for synthesis of Bi_2Se_3.

The deposition bath was prepared in 100 ml beaker by addition of 0.1 M bismuth nitrate solution. Appropriate amount of TEA was added to this solution. Sodium selenosulphate (Na_2SeSO_3) solution was then added to the bath. Ammonium hydroxide solution was used to increase the pH of the solution. The pH of the solution bath was varied from 11 to 13 and the pH was optimized as 12 to obtain uniform Bi_2Se_3 thin films at room temperature. After a deposition period of two hours, substrates were removed from the bath and washed with distilled water and dried.

2.2. Reaction mechanism

Bi_2Se_3 film growth can occurred by two distinct mechanisms: Ion-by-ion and cluster [1,18].

In alkaline medium sodium selenosulfate hydrolyzes to give hydrogen selenide and selenide ions

$Na_2SeSO_3 + OH^- \leftrightarrow Na_2SO_4 + HSe^-$ --------- (1)

$HSe^- + OH^- \leftrightarrow H_2O + Se^{2-}$ -------- (2)

From (1) and (2), the equilibrium constant of HSe^- is predominant in the solution. The concentration of Se^{2-} ions can be increased by addition of the excessive hydroxide ions to facilitate forward reaction.

$[BiN(CH_2\text{-}CH_2\text{-}OH)_3]^{3+} \rightarrow Bi^{3+} + N(CH_2\text{-}CH_2\text{-}OH)_3$ ------ (3)

According to the ion-by-ion mechanism Se^{2-} and Bi^{3+} will condense on the glass substrate as:

$2Bi^{3+} + 3Se^{2-} \rightarrow Bi_2Se_3$ --------- (4)

Glassy Bi_2Se_3 thin films deposited on glass substrates were dark gray in colour, well adherent to the substrates and continuous in appearance.

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2.3. Characterization

The structural properties and crystallinity of the films were analyzed by Schimadzu 6000 X-ray diffractometer using CuKα (λ=1.5418 Å). The optical studies were carried out using UV-VIS-NIR double beam spectrometer in the wavelength range 250-900 nm, in transmittance mode. SEM images were recorded on a JEOL-SEM for the examination of surface morphology of the deposited films. The electrical resistivity of the films was determined in the temperature range 303–463K by employing four probe method. Photocurrents were measured using multifunctional optical power meter. An ELH lamp was used for white light and a series of filters were used for monochromatic light.

3. Results and discussion

3.1. Structural properties

X-ray diffraction pattern of as-deposited and annealed (at 200°C in air for one hour) Bi_2Se_3 thin film of thickness 240 nm are shown in Fig. 1 and Fig. 2 respectively. The film prepared at room temperature (RT) is nearly amorphous in nature while annealed bismuth selenide films exhibit a weak (015) XRD peak (JCPDS file no. 33-0214). The amorphous film coated by chemical bath deposition became polycrystalline (hexagonal structure) on annealing [19,20].

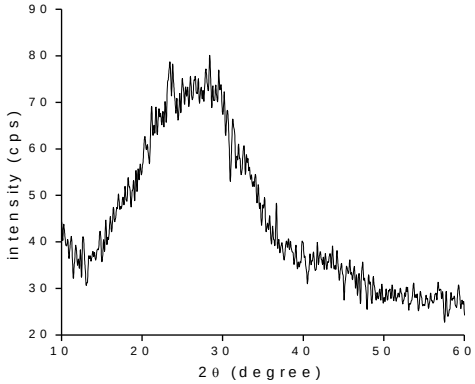

Fig 1. XRD pattern of as-prepared Bi_2Se_3 film.

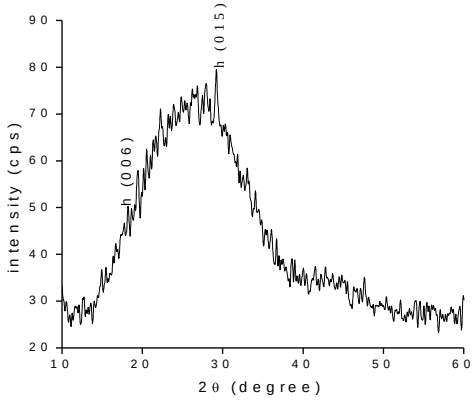

Fig 2. XRD pattern of annealed Bi_2Se_3 film.

The lattice constants were found to be a = 4.16 Å and c = 28.8 Å which are in close agreement with the values reported for bulk (a = 0.4138 and c = 2.8623 nm) and to those reported by Saji etal [21] and Wang et al [22] and the value available in JCPDS data.

The grain size of the crystallites in the annealed film was calculated as 20 nm corresponding to the peak at 2θ=29.24° and 19 nm at 2θ=18.11° using Scherrer's equation. The increase in grain size may be due to the reorientation of grain boundaries when subjected to heat treatment [20].

3.2. Microstructural studies

The SEM photographs of as-deposited and annealed Bi_2Se_3 thin films at the magnifications 10,000X are as shown in Fig. 3 and 4 respectively. SEM micrographs of as-deposited film showed a texture surface and the annealed film images clearly demonstrate the porous surface morphology with spherical grains. The micrographs show total coverage of the substrate surface with clear grains.

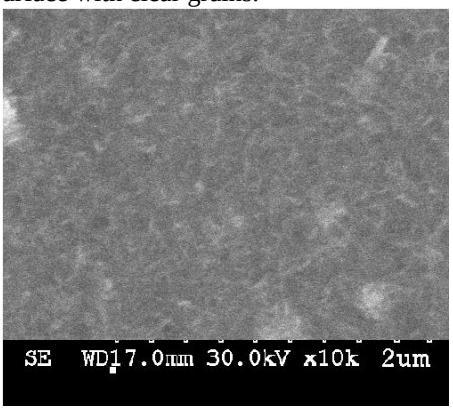

Fig 3. SEM images of as-deposited Bi_2Se_3 film.

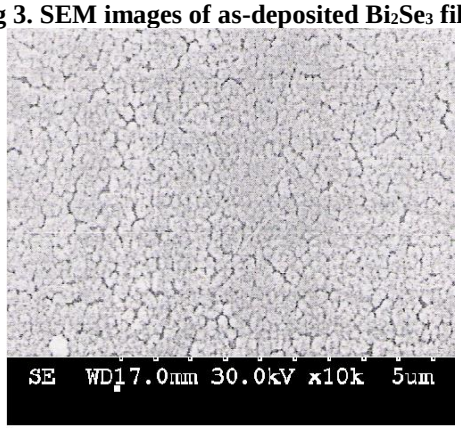

Fig 4. SEM images of annealed Bi_2Se_3 film.

3.3. Optical studies

Optical absorption may help in explaining some features concerning the band structure of these materials. The UV-Vis-NIR spectrum of the prepared and annealed films was recorded in the range of 200- 2500 nm. The plot between wavelength and T (%) is presented in the Fig. 5.

The film prepared at RT has relatively high transmittance. The annealing strongly influences the transmittance of the film. Further the transmittance in the visible region is relatively less when compared with transmittance in the NIR region. Also, annealing shifts the absorption onset to shorter wavelength (blue shift).

The high absorption region was investigated for evidence of either direct or indirect transitions. The direct transition dependence of 'α' on photon energy ($h\nu$) is given by the relation 1:

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \qquad \text{---------- (5)}$$

where A is constant, E_g the energy gap separation between conduction band and valence band The estimated band gap of Bi_2Se_3 thin films (as deposited and annealed) was achieved by plotting of $(\alpha h\nu)^2$ as a function of $h\nu$ as shown in Fig. 6 and Fig. 7. Since the plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for these samples are almost linear, the direct nature of the optical transition in Bi_2Se_3 is confirmed.

Using this linear portion, we calculate the optical energy band gaps by extrapolating the linear segment of the curve as shown in the figure. The direct band gap of as-deposited Bi_2Se_3 (E_g=1.11 eV) decreases to 1.02 eV upon annealing [19,20].

The shift in the absorption edge toward longer wavelength upon annealing, the chemically deposited thin film is associated with an improvement in the crystallinity of the films [23]. In the present case the improvement in the crystallinity of the films upon annealing was evidenced in the XRD studies.

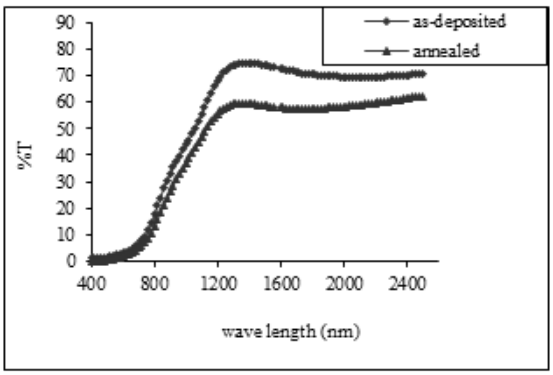

Fig 5. Optical transmitance spectra of Bi_2Se_3 thin films.

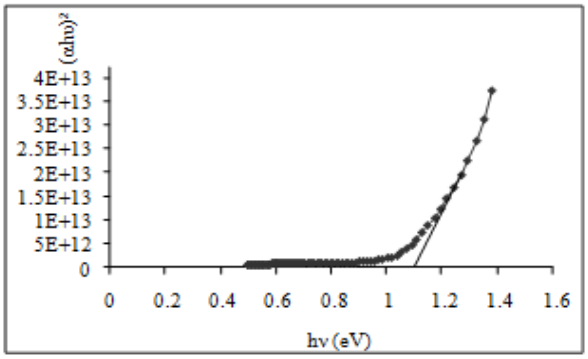

Fig 6. Dependence of $(\alpha h\nu)^2$ on hν for as-prepared Bi_2Se_3 films.

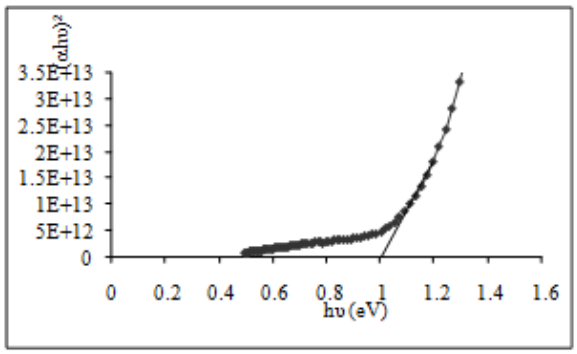

Fig. 7. Dependence of $(\alpha h\nu)^2$ on hν for annealed Bi_2Se_3 films

3.4. Resistivity measurements

The electrical measurements (using four probe method) on as-deposited Bi_2Se_3 films show that its electrical resistivity is approximately 6 kΩ/cm^2. The films are annealed in air for 1hr at 200^{0}C. The resistance – temperature measurements of annealed bismuth selenide thin films behave as a typical semiconductor. With increasing temperature the electrical resistivity decreases according to the relation

$R = C \exp(E_a/2kT)$

Where E_a is activation energy and k is Boltzmann constant. The activation energy was obtained from a plot of the log of electrical resistance versus reciprocal temperature range between 303 and 463K (Fig. 8). As can be seen, from the plot (Fig. 8) lower and higher temperature slopes differ, the slope being related to the activation energy by E_a/2k. The calculated values for the activation energies at low and high temperature regions are 0.18eV and 0.9eV respectively which is in good agreement with earlier reporters [19].

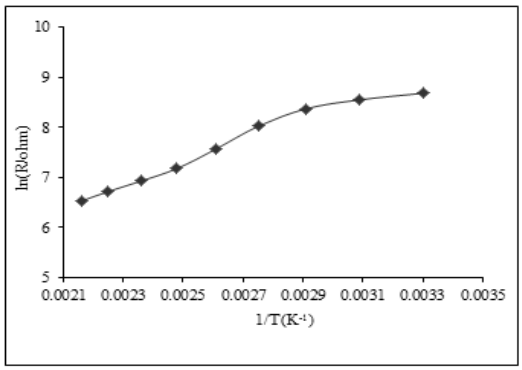

Fig 8. Dependence of logarithm of the electrical resistance on the reciprocal absolute temperature for Bi_2Se_3 thin film

3.5. Photoconductivity studies

The variation of photocurrent with applied voltage is shown in Fig. 9. The photocurrent increases with increase in intensity as well as the applied voltage and is good agreement with earlier workers [24,25]. The observed linear dependence of photocurrent with applied voltage which supports that the deposited films are free from traps.

Fig. 10 shows the variation of photocurrent with applied voltage for as-deposited and annealed Bi_2Se_3 thin films. The as-deposited films were annealed at 200^{0}C for one hour in air. After annealing, the films show a systematic increase in the photocurrent with voltage. The increasing in current is due to improvement in crystallinity of the films, which would increase the charge carrier mobility. Similar behaviour has been reported in the case of chemically deposited bismuth sulphide thin films [26].

The plot of photocurrent vs. wavelength of light for as-deposited and annealed films is shown in Fig. 11 and Fig. 12.

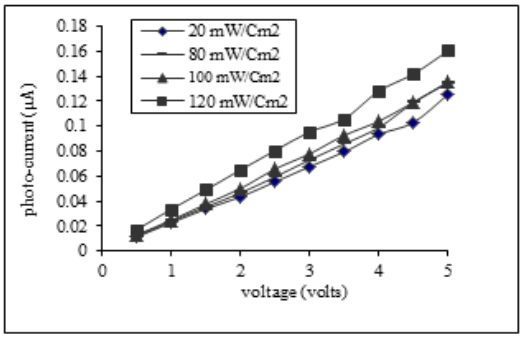

Fig 9. Variation of photo-current with applied voltage.

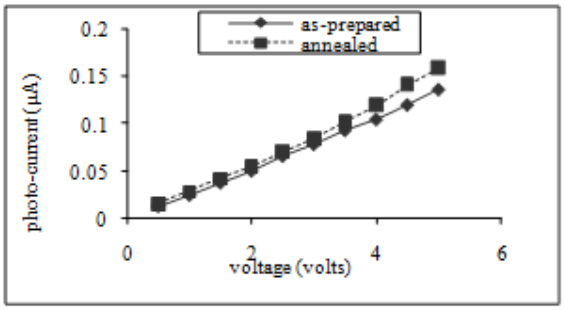

Fig 10. Photocurrent response curves for as-prepared and annealed Bi_2Se_3 films.

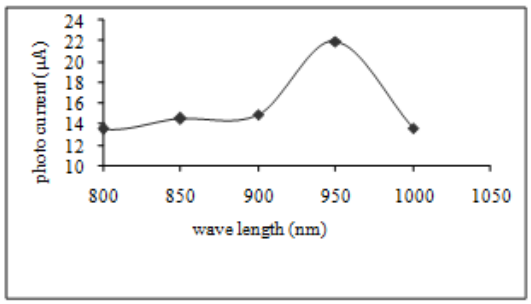

Fig 11. Spectral response of photo-current (as-prepared Bi_2Se_3 film).

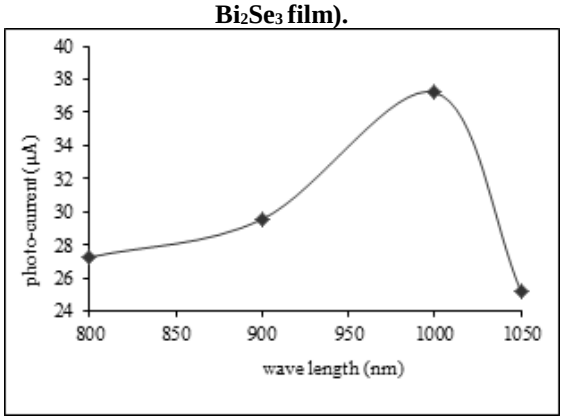

Fig. 12. Spectral response of photo-current (annealed Bi_2Se_3 film)

The photocurrent remains constant up to certain wavelength and attains a maximum and then decreases.

In contrast the spectral response of the annealed Bi_2Se_3 prepared in the study shows the peak around 1000 nm. The photocurrent of the annealed films in the long wavelength region may be associated with structural imperfections but such defect is reduced by annealing [27].

4. conclusions

Chemical bath deposition method (CBD) is employed to prepare Bi_2Se_3 thin films from a bath containing bismuth nitrate and sodium selenosulfate. The as-deposited thin film exhibits amorphous structure and it shows a polycrystalline nature (hexagonal structure) with enhancement in crystallinity upon annealing as indicated by the XRD and SEM studies. Bi_2Se_3 thin films exhibits direct and allowed transition type. The strong optical absorption corresponding to a band gap of 1.11 eV for as- prepared films decreases to about 1.02 eV upon annealing. The resistivity value of approximately $6k\Omega/cm^2$ for as-prepared thin film decreases upon annealing. According to temperature-resistance measurements Bi_2Se_3 thin films are typical semiconductor material upon annealing, with calculated activation energies of 0.18eVand 0.9eV at lower and higher temperature respectively. In photoconduction studies after annealing, the films show systematic increase in the photocurrent with applied voltage than in the as-prepared films. Hence the enhancement in conductivity thus results from improved crystallinity. This may open up various possibilities for the application of these films by chemical bath deposition technique.

Acknowledgment

The authors are thankful to Head, Department of Physics and Dr. T. Balasubramaniam, Kongunadu Arts and Science College for providing laboratory facilities for this work. The authors are grateful to Department of Metallurgy, PSG College of Technology for giving permission to complete XRD studies.

Thanks to Dr. C. Sanjeeviraja, Professor and Head, Department of Physics, Alagappa University, Karaikudi for taking photoconduction measurements. The author acknowledges Coimbatore Institute of Technology (CIT) and Central Electrochemical Research Institute (CECRI), Karaikudi for obtaining SEM and optical studies respectively.

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