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CHARACTERISTICS OF Bi_2S_3 THIN FILMS DEPOSITED BY A NOVEL METHOD

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Thin films of bismuth sulphide (Bi_2S_3) are deposited by a novel nebulised spray pyrolysis technique. The deposited films are characterized by X-ray diffraction, Scanning Electron Microscopy, EDAX, UV-Vis. Spectroscopy. Electrical and photoelectrochemical properties of the films are analysed by four probe resistivity and C-V measurements respectively. As-deposited films are amorphous and annealing of the films is found to improve the crystallinity of the film. Optical transitions involved in the material are found to be direct and allowed. The films recorded a room temperature resistivity of 20 Ω-m.

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1. Introduction

Bismuth trisulphide (Bi_2S_3) is a potential material for electrochemical photovoltaic cells. Bi_2S_3 has suitable band gap (1.7 eV), high absorption coefficient in the visible region and it is a low cost material which is also non-toxic. In view with the importance of the material in solar photovoltaics the material has been deposited by number of methods such as chemical bath deposition[1], electrodeposition[2], SILAR[3], thermal evaporation[4], reactive evaporation[5] and spray pyrolysis[6]. Spray pyrolysis is a versatile technique which can be used for the efficient deposition of thin films. Microstructure of the films deposited by spray pyrolysis depends very sensitively in the following on spray head geometry, carrier gas and liquid flow pattern and rate, droplet velocities, sizes and geometries, nature and temperature of the substrate, the kinetics and thermodynamics of pyrolytic reaction and the temperature profile during the deposition process [7]. Thin films having uniform microstructure may be obtained by using an aerosol of the spray solution consisting of very fine and uniform droplets. Atomizers employing different techniques have been adopted for the preparation of aerosols such as air blast, ultrasonic and electrostatic. In the present work an attempt has been made to deposit device quality Bi_2S_3 thin films by using a novel atomizer. To the best of the knowledge of the authors this is the first report on the deposition of Bi_2S_3 thin films by nebulised spray pyrolysis technique.

2. Experimental

In the present work novel 'small volume jet nebulizer' is used for the production of uniform and very fine aerosol. It contains a small nebulising chamber with a narrow orifice. Jet nebulizers form aerosols by using a compressor to deliver a pressurized jet stream of air down a narrow tube and through a narrow opening. The result is a drop in pressure that creates a vacuum (venturi effect), forcing the liquid to come up from a reservoir. Small droplets of liquid created in this manner are propelled out of the device by the jet stream. The solution entertained in the reservoir is made as an aerosol consisting of very fine and uniform droplets. The special feature of

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the small volume jet nebuliser is that it consists of a baffle which is placed in the aerosol stream. The baffle controls the size of the droplets in such a way that only very fine droplets are allowed to escape the orifice and those larger droplets are returned to the reservoir itself. The resulting droplet size distribution contains aerosol of uniform droplets. Specially designed spray gun is used for the deposition of thin films by nebulised spray pyrolysis.

Bismuth nitrate ($Bi(NO_3)_2$) and thiourea ($CS(NH_2)_2$) are used as the precursor for bismuth and sulphur ions respectively. The spray solution is prepared by dissolving appropriate amount of material in deionised water. Equimolar solution (0.2 M) of the precursors are mixed in appropriate volume to obtain Bi:S ratio as 2:3. Compressed air at a pressure of 1 bar is used as the carrier gas. The substrate is heated to a predetermined substrate temperature of 300°C. The films are obtained by spraying the spray solution on the preheated substrates. The solution is sprayed intermittently in order to avoid excessive cooling of the substrate due to continuous spraying. The substrates are allowed to cool down to the room temperature naturally. The deposited films are annealed at 300°C for an hour.

Bi_2S_3 thin films deposited by nebulised spray pyrolysis technique are characterized by X-ray diffraction, Scanning Electron Microscopy, Atomic force Microscopy, Energy Dispersive Analysis, UV-Vis. spectroscopy and Four probe resistivity. Thickness of the films is measured using Mitutuyo Surface Profilometer (Surf Test 330). Panalytical X-ray diffractometer (X-pert Pro) is used for recording the X-ray diffraction pattern of the films. The Surface morphology and elemental composition of the films are analysed using Scanning Electron Microscope (JEOL JSM 5600) with Energy Dispersive X-ray Spectrometer (INCA Oxford). UV-Vis-NIR double beam spectrophotometer (JASCO V-570) is used to record the optical transmittance spectra of the films. Four probe resistivity set up with Keithley electrometer is used for the resistivity measurement.

3. Results and discussion

X-ray diffraction pattern of the as-deposited and annealed thin films are shown in figure 1. No significant peaks are observed in the case as-deposited film which indicates the amorphous nature of the films. Prominent peaks are observed in the case of annealed film which indicates the polycrystalline nature of the films. The peaks are indexed by comparing the peak position and relative intensities with standard data (JCPDS card no. 75-1306). Films are crystallized in bismuthinite phase of bismuth sulphide having orthorhombic crystal structure. No peaks corresponding to metallic bismuth or sulphur are found and hence it is concluded that the deposited material is of single phase. X-ray diffraction analysis of the films indicates that it is possible to obtain single phase Bi_2S_3 films by nebulised spray pyrolysis.

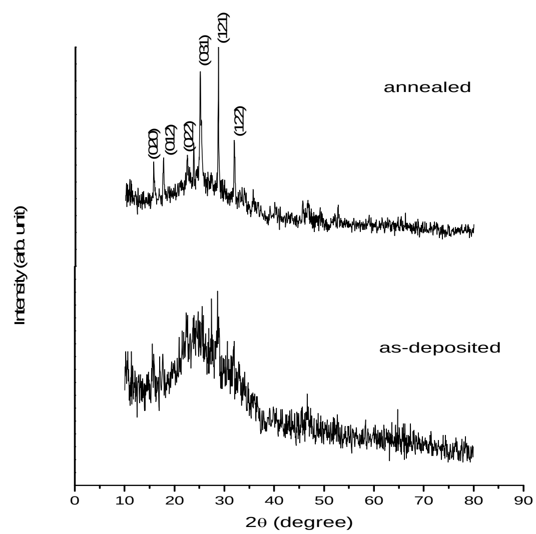

Fig. 1 XRD pattern of as-deposited and annealed Bi_2S_3 thin films

Scanning electron micrographs (figure-2) of the film reveals the formation of uniform films and the films has no pin holes or voids. Novel splice like grains are observed in the case of Bi_2S_3 thin films deposited at a substrate temperature of 300°C. The size of the slice shaped grains is deduced from SEM micrograph using the software "Image J". The average diameter of the slice shaped grains was found to be 0.25 μm.

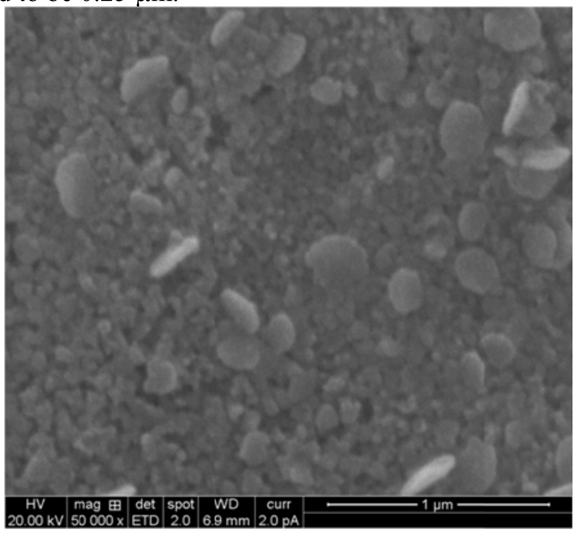

Fig. 2 Scanning electron micrograph of Bi_2S_3 thin film deposited by nebulised spray pyrolysis technique

Energy dispersive X-ray analysis is performed to ascertain the elemental composition of Bi_2S_3 thin films deposited by nebulised spray pyrolysis. EDAX spectrum of the film is shown in figure 3. It is found that the Bi_2S_3 thin films deposited by nebulised spray pyrolysis are stoichiometric in nature.

Optical transmittance of the films is recorded in the wavelength range of 350-1200 nm. The films exhibited higher transmittance in the NIR region of the electromagnetic spectrum. Transmittance of the films falls of rapidly in the visible region which indicates that the absorption of film is high in this region. Optical transmittance spectrum of the film is shown in figure 4. Absorption coefficient of the film is calculated from the transmittance (T) data using the relationship

$$\alpha = (1/t)*\ln(1/T)$$

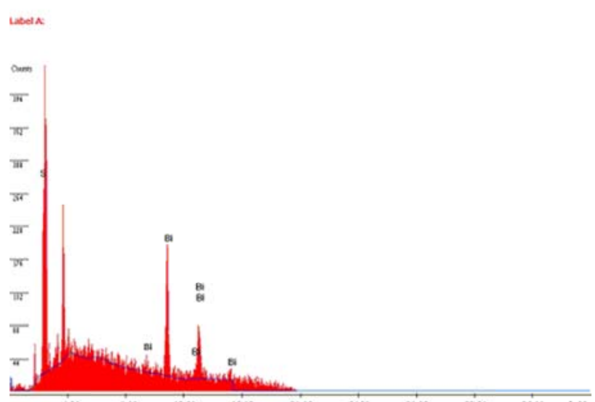

Fig. 3 EDAX spectrum of Bi_2S_3 thin film.

where't' is the thickness of the film. The optical band gap energy of the films is calculated using the classical relationship for near edge optical absorption in semiconductors

$$\alpha h\nu = K\,(h\nu - E_g)^{n/2}$$

where K is a constant, hν is photon energy, E_g is the optical band gap and 'n' is a constant equal to 1 for direct band gap and 4 for indirect band gap compounds. Plot of $(\alpha h\nu)^2$ vs. hν of Bi_2S_3 thin films is shown in figure 5.

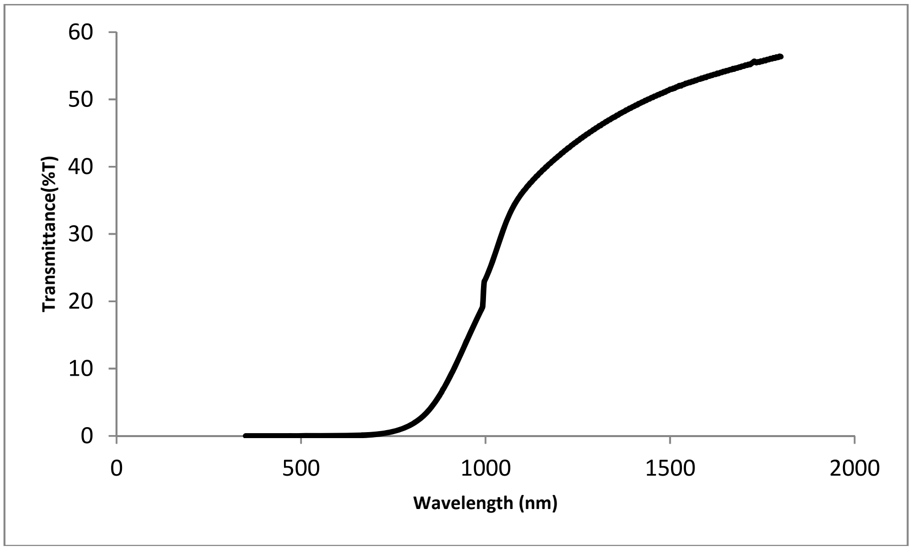

Fig. 4 Transmittance spectra of Bi_2S_3 thin film deposited at a substrate temperature of 300°C

Linear nature of the plot in the highly absorbing region reveals that the optical transitions taking place in the film are direct and allowed. The extrapolation of the linear part of the plot to the energy axis gives the optical band gap value of the film which is 1.6 eV. Resistivity of the films is measured by four probe resistivity set up. Resistivity of the films is recorded in the temperature range of 27°C-150°C.

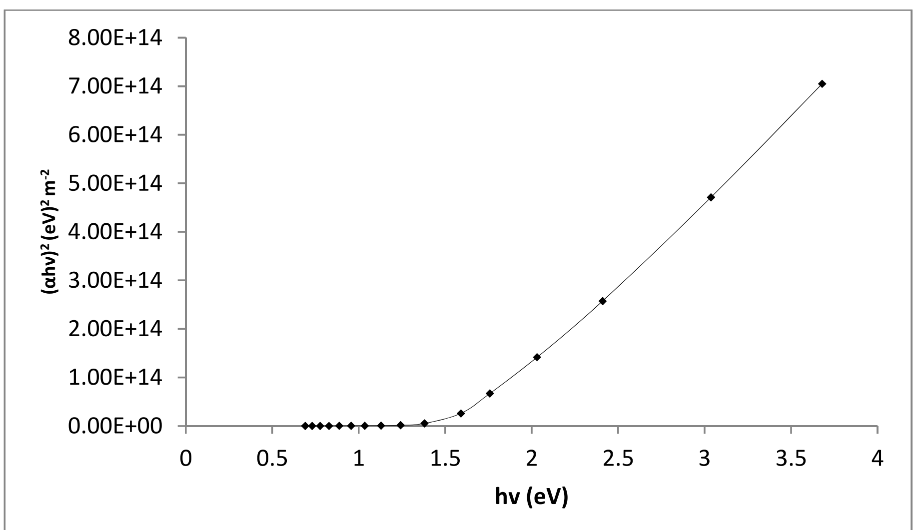

Fig. 5 Plot of $(\alpha h\nu)^2$ vs. hν of Bi_2S_3 thin film deposited at 300°C.

The resistivity of the film decreases with increase in temperature there by indicating the semiconducting nature of the films. The room temperature resisitivity of Bi_2S_3 thin film deposited at a substrate temperature of 300°C is 20 Ω-m. The electrical resisitivity of the semiconducting film is governed by the Arrhenius relation

$$\sigma_{d.c.} = \sigma_0\, e^{-Ea/kT}$$

where E_a is the activation energy for d.c. conduction, k is the Boltzmann constant and σ_0 is the pre-exponential factor. The Arrhenius plot of the Bi_2S_3 thin films is shown in figure 6.

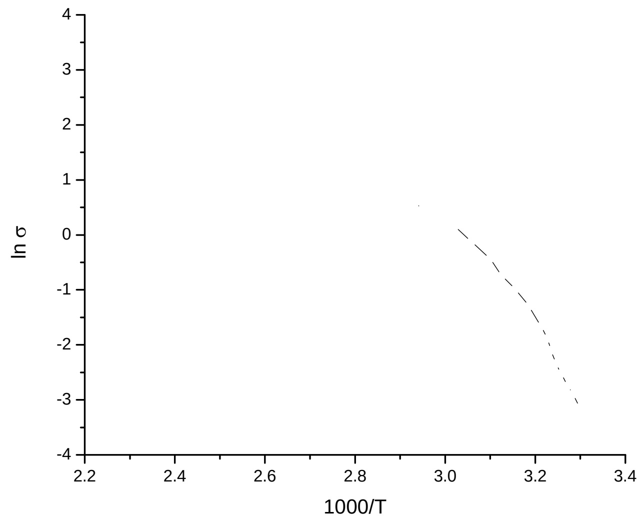

Fig. 6 Arrhenius plot of Bi_2S_3 thin films deposited by nebulised spray pyrolysis

4.Conclusion

Thin films of Bi_2S_3 are deposited by nebulised spray pyrolysis using bismuth nitrate and thiourea. Films are deposited at a substrate temperature of 300°C. The as-deposited films are amorphous in nature while the annealed films are polycrystalline. The films are crystallized in the bismuthinite phase of bismuth sulphide. The analysis of surface morphology of the films indicates the novel microstructure of the film. The films are found to be stoichiometric and the presence of either excess bismuth or sulphur is not observed. The optical transition taking place in the film is found to be direct and allowed.The calculated direct optical band gap of the films is 1.6 eV. The temperature dependence of resistivity revealed the semiconducting nature of the film.

Acknowledgement

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