

Optical and Electrical Properties of Doped and Undoped Bi₂S₃–PVA Films Prepared by Chemical Drop Method

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Received January 5th, 2011; revised January 24th, 2011; accepted February 2nd, 2011.

ABSTRACT

Bismuth sulfide was prepared in PVA matrix by chemical method using solutions of $Bi(NO_3)_3$ and Na_2S . Bi_2S_3 was doped during preparation using Br_2 vapour and also liquid drops of Br_2 . Both doped and undoped Bi_2S_3 –PVA films were characterized by SEM, XRF, optical absorption and electrical conductivity measurements. The undoped films consisted of particles of sizes 156 nm-184 nm as revealed by SEM micrographs. The films doped with Bromine (Br_2) vapour were found to consist of rods of diameters ranging from 75 nm to 80 nm. The films doped with Br_2 liquid drops showed rods of diameters ranging from 4843 nm to 6930 nm. XRF spectra confirmed the presence of bismuth, sulfur and bromine in the doped films. The temperature variation of doped and undoped films in the temperature range from 298 K to 383 K shows more or less similar pattern of variation with two regions of conduction. The band gap obtained from the absorption spectra was found to change from 3.61 eV to 3.78 eV and the absorption edge shifted towards the lower wavelength with decrease in diameter of the particles or rods.

Keywords: Nanostructures, Doping, Bismuth Sulfide, Semiconducting Materials, Solar Cells

1. Introduction

The members of the V-VI group of compound semiconductors are technically important materials because of their photosensitivity, photoconductivity and thermoelectric power [1,2]. Bismuth sulfide (Bi₂S₃) is an important member of V-VI group of compound semiconductor and it is a direct band gap material. The earlier reported [3] band gap of bulk Bi₂S₃ is 1.3 eV. The more recent value of band gap is reported to be in the range 1.3-1.7 eV [4], which lies in the visible solar energy spectrum. It has large absorption coefficient [5]. Thus it is an ideal candidate for solar cells and photodetectors in the visible wavelength region. Due to its significant thermoelectric effect, this material is important in thermoelectric applications [6]. The excellent electrochemical hydrogen storage properties of Bi₂S₃ flower like patterns with well aligned nanorods and discs like Bi₂S₃ nanorods networks have been investigated by Xie and Qi groups respectively [7,8]. Bi₂S₃ is a layered semiconductor that crystallizes in the orthorhombic system and is iso structural to antimony sulfide (Sb_2S_3) and selenide (Sb_2Se_3) [3]. Bi₂S₃ thin films

have been reported to be prepared by many workers following different chemical routes and using different complexing agents and sulfide sources [9-11]. Recently considerable researches have been carried out focusing on the synthesis of one dimensional (1D) microstructures of Bi₂S₃. Depending on growth condition, different 1D structure such as nanotubes [12], nanowires [13,14], nanorods, nanoflowers [15] and, nanoribbons of Bi_2S_3 have been reported to be synthesized by different research groups. In addition to 1D, two dimensional (2D), and three dimensional (3D) nanostructures of Bi₂S₃ can be obtained via physical and chemical methods but the control of size and shape of the structures remain as a difficult task. The importance of one dimensional material is that as the diameter of the semiconductor approaches the exciton Bohr diameter, its electronic properties changes (Quantum size effect). This can be observed as a blue shift in the optical band gap or excitation energy.

In the present communication, we have reported the preparation of Bi_2S_3 within the self organized pores of Poly vinyl alcohol (PVA) via chemical drop method. Thin films of Bi_2S_3 were then doped with bromine. Both

doped and undoped films were characterized for their structural, optical and electrical properties.

2. Experimental Details

Thin films of Bi₂S₃-PVA were deposited on glass substrates using PVA as matrix, Bi(NO₃)₃ and Na₂S as Bi³⁺ and S^{2-} ion source respectively. All chemical products used in this work were of analytical grade. They were used without further purification. First the matrix solution was prepared by mixing 5 wt% of PVA in double distilled water and stirred in a magnetic stirrer at a constant temperature until a transparent solution was obtained. To this solution, 0.01 M (molarity) of Bi(NO₃)₃ was added in the ratio of 2:1 and the stirring was continued at the same temperature for three hours and then brought down to the room temperature (300 K). To the transparent solution obtained, 0.03 M of Na₂S was added drop by drop until the solution turned into dark brown. The resultant solution was kept in dark undisturbed for 12 hours for stabilization. This solution was then cast over glass substrates drop by drop and dried at room temperature (300 K). This way undoped Bi₂S₃-PVA films were obtained. Doped Bi₂S₃-PVA were obtained by passing bromine (Br₂) while adding 0.03 M Na₂S to the transparent solution containing Bi(NO₃)₃ and PVA at room temperature and stirred for half an hour.

The thicknesses of the films were measured by multiple beam interferometer technique. Surface morphological studies of the chemically deposited Bi_2S_3 –PVA thin films were done using Scanning Electron Microscope (LEO 1430 VP) operating with an accelerating voltage 15 kV. X-ray fluorescence study (XRFS) was done using Axios XRF spectrometer for elemental analysis of the as prepared doped films. Optical absorption studies were carried out using a UV-visible spectrophotometer (Hitachi U-3210) in the wavelength range 350-750 nm.

The electrical conductivity measurements of the films were done using two coplanar Aluminium (Al) electrodes separated by a small gap. These electrodes were vacuum deposited at the two ends of the rectangular Bi_2S_3 –PVA strip. The deposition of electrodes was performed at a reduced pressure of 10^{-5} Torr in a vacuum deposition unit (VICO-12). The conductivity of Bi_2S_3 –PVA was determined by measuring the resistance of the samples using an electrometer (Keithley 6514) in the temperature range 298 K - 383 K and the same temperature was varied using a temperature controller. Temperature of the samples was measured by means of a thermocouple.

3. Results and Discussion

3.1. SEM Analysis

Figure 1 shows the SEM photograph of a film containing

undoped Bi₂S₃ embedded in a PVA matrix. From the photograph it is observed that the distributions of grains are not uniform throughout the PVA matrix. But the film is smooth without any visible pores or cracks. The grain size is found to be in the range 156-183 nm. Figure 2 shows the SEM photograph of Bi2S3 doped with bromine vapour which shows rod shaped structures of diameters in the range 78-80 nm (nanorods). The rods are not distributed uniformly throughout the matrix. Figure 3 shows SEM photograph of Bi₂S₃ doped with bromine liquid drops. The figure reveals rod like structures with diameter in the range 4843-6930 nm (microrods) distributed unevenly throughout the PVA matrix. The rods doped with Br₂ is dispersed in PVA matrix whose conductivity is very low and hence concentration could not be measured by conventional methods. The doping was performed using MERCK made 99.99% pure Br₂. The thickness of undoped Bi₂S₃-PVA film was 8×10^{-5} m, while doped films consisting of nanorods and microrods were 3 $\times 10^{-5}$ m and 7×10^{-5} m thick respectively.

3.2. X-Ray Fluorescence (XRF) Studies

The Figures 4(a) and 4(b) show the XRF spectra of doped



Figure 1. SEM image of undoped Bi₂S₃ in PVA matrix.



Figure 2. SEM image of bromine doped Bi_2S_3 nanorods in PVA matrix.



Figure 3. SEM image of bromine doped Bi_2S_3 microrods in PVA matrix.



Figure 4. XRF spectra of doped Bi_2S_3 nanorods in PVA matrix.

Bi₂S₃-PVA films. The spectrum in **Figure 4(a)** exhibits the prominent peaks of BrK β , BiL β , BrK α and BiL α 1 lines showing the presence of Bi and Br in the prepared

film. The spectrum shown in **Figure 4(b)** shows the peaks of BiM β , BiM α 1 and SK α lines along with the lines of ClK α , RhL α and PK α . Peaks for Cl, Rh and P appear from the target used in the XRF instrument and from the possible impurities present in the glass substrates.

3.3. Optical Absorption Studies

The optical (electronic) properties of semiconducting compounds result from band structures of semiconducting materials and are very important in a large number of applications. Figure 5 shows the absorbance spectra of doped and undoped Bi₂S₃-PVA films. From the spectra the absorbance edge for undoped Bi₂S₃ is found to occur at 400 nm and the same has been found to occur at 377.7 nm and 422 nm for Bi₂S₃ doped with Br₂ vapour and Br₂ liquid respectively. An extra absorption peak at 370 nm which corresponds to 3.35 eV has been observed in the film doped by Br₂ vapour. The extra peak showed in nanorods doped by Br₂ vapour has been thought to be due to some defects which were crept in to the films during preparation. This peak has been found to disappear on aging of the films. The nature of transition (direct or indirect) involved can be determined considering the relation of absorption coefficient

$$\alpha = a \frac{\left(hv - E_g\right)^n}{hv} \tag{1}$$

where "*a*" is constant, E_g is the separation between the conduction band and valence band. The absorption coefficient α is calculated from the relation [16]

$$\alpha = 2.303 \frac{A}{t} \tag{2}$$

where A is the absorbance and t the film thickness. In all the three samples, the plots of $(\alpha hv)^2$ vs (hv) are linear as shown in **Figure 6** indicating that the transition is a direct band gap edge transition. The extrapolation of the linear portion of such a plot to $\alpha = 0$ yields the band gap energy. The band gap so obtained for undoped Bi₂S₃ particles is 3.70 eV while the doped Bi₂S₃ nanorods have a band gap value 3.78 eV and that of the doped Bi₂S₃ microrods is 3.61 eV.

3.4. Electrical Conductivity

The variation of electrical conductivity of doped and undoped Bi_2S_3 -PVA films measured in the 298 K-383 K temperature range are shown in **Figure 7**. The conductivity was observed to increase rapidly in all the three samples as the temperature was raised from 298 K attaining a maximum around 322 K, after which the conductivity was found to decrease and reached a minimum around 342 K beyond which the conductivity showed an



Figure 5. UV-absorption spectra of doped and undoped Bi_2S_3 -PVA films.



Figure 6. Energy band determination of doped and undoped Bi₂S₃-PVA films from $(ahv)^2$ vs (hv) plot.



Figure 7. Variation of log (σ) vs 1/T for doped and undoped Bi₂S₃–PVA thin films.

increase again. The nature of variation of conductivity of PVA film alone with temperature is found to be similar as reported in our earlier paper [17] and by Ahmed and Abo-Ellil [18]. Thus the nature of variation of Bi_2S_3 -PVA films is dominated by the conductivity variation of the PVA matrix. The value of conductivity of undoped and doped Bi₂S₃-PVA films are given in Table 1.That doping occurred in Bi₂S₃ is indicated by the increase of conductivity in nanorods and microrods. Such rods like structures of Bi₂S₃ have been reported by some other workers [19-21]. It is not however, understood as how the rods like structures were initiated in the process of doping. The probable mechanism for the formation of rods may be due to preferential growth in certain direction initiated by dopant material. Growth of rod like structure has also been reported by Zhou et al. [22] in undoped Bi₂S₃.

The $\ln\sigma$ versus 1000/T plots for the doped and undoped Bi₂S₃-PVA films depict two conduction regions. These regions have different activation energies which were calculated using the relation

$$\sigma = \sigma_0 e^{-\frac{E_a}{2kT}} \tag{3}$$

where, *Ea* is activation energy, σ_0 is a constant, *k* is Boltzmann's constant and *T* is absolute temperature. Different activation energies indicate different conduction processes such as electronic and ionic conduction [23]. Activation energies for doped and undoped Bi₂S₃– PVA films are tabulated in **Table 1**.

4. Conclusions

Undoped Bi_2S_3 -PVA films were prepared and found to consist of grain sizes in the range 158-183 nm. Bi_2S_3 -PVA films with nanorods and microrods were obtained on doping with Br_2 vapour and Br_2 liquid respectively. The band gap energy was maximum in case of doped Bi_2S_3 -PVA nanorods and minimum in case of Bi_2S_3 -PVA microrods. Thus the band gap energy has been found to

Table 1. Electrical conductivity and activation energy values of Bi_2S_3 -PVA thin films.

Sample	$\begin{array}{c} \text{Room temperature} \\ \text{conductivity} \\ 10^{-5} \times (\Omega^{-1} \cdot m^{-1}) \end{array}$	Activation energy (eV)	
		Region I	Region II
Undoped Bi ₂ S ₃ -PVA	0.28	0.397	0.999
Doped Bi ₂ S ₃ –PVA (Microrods)	2.46	0.345	0.746
Doped Bi ₂ S ₃ -PVA (Nanorods)	7.91	0.37	0.539

increase with decrease in size showing a blue shift in the absorption spectra. On doping there was an increase in the electrical conductivity of Bi_2S_3 -PVA films. However the conductivity of all the samples was largely influenced by the conductivity of PVA structure.

5. Acknowledgements

The authors express their gratefulness to the Department of Chemistry, Gauhati University, Guwahati and IIT Guwahati for providing us the UV-Visible Spectra and SEM facilities respectively.

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