Thermally Deposited Sb$_2$S$_3$: Bi Thin Films for Solar Cell Absorber

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**Abstract:** In recent years there has been growing interest in the materials suitable for real time storage application. Sb$_2$S$_3$ is a prospective material in this regard due to good photoconductivity. In this context, thin films of Sb$_2$S$_3$ and Bi$^{3+}$ doped Sb$_2$S$_3$ were deposited onto the transparent glass substrate by thermal evaporation method. The structural, optical and electrical properties were investigated by XRD, UV-Visible, Photoluminescence, and Impedance spectroscopic techniques. The XRD patterns confirm the orthorhombic crystal structure of Sb$_2$S$_3$ and the inclusion of Bi$^{3+}$ ions in the crystal system. UV-Visible analysis exhibited wide optical absorption in the visible region for both Sb$_2$S$_3$ and Bi$^{3+}$ doped films and their band gap energy was found to be 1.60 eV and 1.55 eV respectively. The photoluminescence spectra showed a strong emission at 361 nm. The value of capacitance, dielectric constant and real part of impedance decreases with increase in doping concentration [8, 9]. E. Ca´rdenas-Valenzuela et al., 2016 studied the optical properties of Ni doped Sb$_2$S$_3$ thin films and found that the bandgap increases with increase in Ag concentration [6]. N. J. Mathew et al., 2011 studied the dielectric and impedance properties of Se doped Sb$_2$S$_3$ thin films and found that the bandgap increases with increase in doping [7]. S. Muataq et al., 2016 studied the optical properties of Ni doped Sb$_2$S$_3$ thin films and Sn doped Sb$_2$S$_3$ thin films found that the bandgap energy increases with increase in doping concentration [8, 9]. E. Ca´rdenas

**Keywords:** antimony sulfide, bismuth, thin film, dielectric

1. INTRODUCTION

Binary and ternary chalcogenides of Sb$_2$S$_3$ are promising materials for electronic devices applications especially in photoconductive target for the videocon type of television camera tubes, microwave, switching and optoelectronic devices. Sb$_2$S$_3$ thin films are used in solar energy conversion and thermoelectric cooling technologies [1] among the available chalcogenides. Sb$_2$S$_3$ has attracted much attention due its unique properties such as high optical absorption coefficient, optimum band gap (E$_g$ = 1.8 eV), high refractive index, well-defined quantum size effects, this material exhibit structural modification when irradiated by light and by an electron beam, their photosensitive and thermoelectric properties. There is a number of reports on the structural and optical properties of Sb$_2$S$_3$ thin films prepared by various techniques such as spray pyrolysis [2], Thermal evaporation [3], chemical bath deposition method [4]. Among the deposition method, the thermal vacuum evaporation technique is relatively simple method to prepare homogeneous Sb$_2$S$_3$ thin films. Extensive research has been done on the deposition and characterization of Sb$_2$S$_3$ semiconducting thin films due to their potential application in the area of optoelectronic device fabrication and microwave. Sb$_2$S$_3$ thin films have good optical transmittance, wide band gap and electrical properties suitable for their application to solar cell fabrication [5]. The properties of Sb$_2$S$_3$ can be tuned for desired applications. Doping is the suitable way to tune the physical properties of Sb$_2$S$_3$ thin films. S.S. Salim et al., 2010 prepared Ag doped Sb$_2$S$_3$ thin films and observed decrease in band gap with increase in Ag concentration [6]. N. J. Mathew et al., 2011 studied the dielectric and impedance properties of Se doped Sb$_2$S$_3$ thin films and found that the bandgap increases with increase in doping [7]. S. Muataq et al., 2016 studied the optical properties of Ni doped Sb$_2$S$_3$ thin films and Sn doped Sb$_2$S$_3$ thin films found that the bandgap energy increases with increase in doping concentration [8, 9].

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et al., 2009 studied the electrical properties of Carbon doped Sb$_3$ thin films [10]. Hence it is noticed that the doping of metals in Sb$_3$ thin films tunes the optical and electrical materials of the Sb$_3$ thin films. Also it is noticed that Bi doped Sb$_3$ thin films not explored well elsewhere. Therefore, it is motivating to prepare pure Sb$_3$ and Bi doped Sb$_3$ thin films by thermal vacuum evaporation technique and to study its opto structural characteristics.

2. EXPERIMENTAL DETAILS

Microscopic glass slides size (76 mm x 26 mm x 1.15 mm) was cleaned well with chromic and then the slides were cleaned with detergent solution. The substrates were adopted by the earlier report [11]. The substrates were once again washed by distilled water and then dried in air. AR grade of antimony sulfide (99.999% purity) and Bismuth (99.999% purity) was purchased from the Merck company were used as starting materials. Antimony sulfide (90% wt ratio) and bismuth powder (10% wt ratio) was pelletized by applying 5 ton of pressure using hydrolic press. The pellet was kept in the molybdenum boat. Prior to evaporation, the pellet was carefully degassed at lower temperature for 45 minutes. The current supply was slowly increased and maintained 90 amp for complete evaporation of the sample. The pressure inside the champer was maintained about 2x10$^{-5}$ Torr. A similar process was adopted for the preparation of (Bi)$_x$(Sb$_3$)$_{1-x}$ thin films (x=0.1; 0.2; 0.3). The Bi doped Sb$_3$ thin films were brown in colour. The deposited films were annealed at 250°C for 1 h in air atmosphere. The thickness of the film was calculated by using the standard procedure [6].

The structural characteristics were carried out by analyzing the XRD patterns obtained using CuKa radiation ($\lambda$=1. 5406Å) in an X'pert PRO X-ray diffractometer. The optical measurements were performed using Hitachi U3400 UV-Vis spectrometer. The photo luminescence spectra measurements are carried out by using PERKIN ELMER LS45. Dielectric measurements were taken for the thin films in the frequency range from 50 Hz – 5 MHz by using impedance analyser using CH instruments CHI60E electrochemical analyzer.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns Sb$_3$ and Bi doped Sb$_3$ films of annealed at 250°C for 1 hr. In Fig.1, a crystalline peaks observed at d-spacing 2.7646Å and 1.4397Å corresponding to (221) and (271) planes respectively of orthorhombic structured Sb$_3$. The diffraction peaks are well matched with the standard Sb$_3$ [JCPDS card no: 06-0474] and similar results were reported for the Sb$_3$ [3, 12].

Fig 1 (b-d) represents the XRD patterns of Bi doped Sb$_3$ thin films. The intensity of the plane (221) is decreased with increase in Bi concentration which indicates the deterioration in the film property. When introducing Bi into Sb$_3$ pattern due to the strain produced in the lattice. These observations confirm the incorporation of Bi atoms in the lattice structure of Sb$_3$. The observed peaks at 66.24° corresponding to the plane (5 2 2) orthorhombic structured Bi$_{1-x}$Sb$_{0.6}$S$_3$ (JCPDS Card No 361229). The Bi$_{1-x}$Sb$_{0.6}$S$_3$ peaks in the XRD results confirm the blend of Bi into Sb$_3$.

The diffraction result also reveals that the incorporation of Bi$^{3+}$ ions does not change the crystal structure of the Sb$_3$ host lattice. Since, the ionic radius of Bi$^{3+}$ (1.17Å) is larger than that of Sb$^{3+}$ (0.90 Å), it is impossible for Bi$^{3+}$ to act as interstitial ions in the Sb$_3$ host matrix. The Bi$^{+}$ can only replace Sb$^{3+}$ substitutionally in the Sb$_3$ lattice sites. Figure 2 shows the peak shift of plane (221) toward the lower angle because the ionic radius of Bi$^{3+}$ (1.17Å) is higher than that of Sb$^{3+}$ (0.90 Å).

The average crystallite size and micro structural parameters such as dislocation density (δ) and micro strain (ε) of undoped Sb$_3$ and Bi doped Sb$_3$ were calculated using the following equations. Debye – Scherrer relation equation as follows [13].

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

(1)

Where, $D_{\text{lat}}$ is the mean grain size of ordered (crystalline) domains(nm), $\lambda$ is the wavelength of characteristics X-rays (Å), $\beta$ is the Bragg diffraction angle of the respective diffraction peak, $\theta$ is the full width at half maximum of the peak and K varies with (h k l) and crystallite shape but usually equal to 0.94.

Dislocation Density (δ) and Micro Strain (ε) can be calculated by...
the following formula \[14, 15\]

\[
\delta = \frac{1}{D^2} \quad \text{(2)}
\]

\[
\varepsilon = \frac{(\beta \cos \theta)}{4} \quad \text{(3)}
\]

From the table it is found that the crystallite size increases with increase in doping except for 0.3% Bi concentration. This decrease in crystallite size for 0.3Bi doping may be caused by the enhanced incorporation of Bi\(^{3+}\) ions into the Sb\(^{3+}\) sites of the host Sb\(_2\)S\(_3\) lattice. The decrease of crystallite size means deterioration of crystalline quality of Sb\(_2\)S\(_3\) films with Bi doping and an increase of total grain boundary fraction in the films, which can enhance grain boundary scattering, thus, result in an increase of electrical resistivity \[16\].

Figure 3 shows the SEM images of pure and Bi doped Sb\(_2\)S\(_3\) thin films. From the figure it is found that the films are uniform and smooth surface.

Figure 4 shows the optical absorption spectra of Sb\(_2\)S\(_3\) and Bi doped Sb\(_2\)S\(_3\) thin films. The Sb\(_2\)S\(_3\) thin film showed wide band of absorbance within the visible region while, Bi doped Sb\(_2\)S\(_3\)sample has higher absorbance between 400 – 500 nm. The spectra also showed a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in a photo electrochemical cells. Doping content reduces the broadness of the peak, may be due to the rearrangement of ions into lattice. From the absorbance spectra, the absorption coefficient \(\alpha\) at each energy \(h\nu\) can be evaluated. The optical absorption studies are very useful to identify the band gap, refractive index, extinction coefficient etc. The absorption coefficient is calculated from the relation equation (1).

\[
\alpha = \frac{2.303}{t \log 1/T} \quad \text{(4)}
\]

where, \(\alpha\) is the absorption coefficient, \(t\) is the thickness of the thin film, \(T\) is the transmittance of the material. The absorption coefficient \(\alpha\) is related to the energy gap \(E_g\) according to the Tauc equation (5)\[7\],

\[
(\alpha h\nu) = A(h\nu-E_g)^n \quad \text{(5)}
\]

where, \(A\) is a constant that depends on the transition probability, \(h\) is the planck constant and \(n\) is equals \(\frac{1}{2}\) for direct band gap. The high absorbance exhibited by this material makes it a potential absorber material in devices for photovoltaic conversion of solar energy. The absorption coefficient was found to be about \(10^5\) cm\(^{-1}\) and it is well agreed with the earlier reports on amorphous Sb2S3 thin films prepared by vacuum evaporation method \[17\].

The band gap \(E_g\) was determined by extrapolating the linear portion of the \((\alpha h\nu)^2\) vs \(h\nu\) curve to intercept the horizontal photon energy axis as shown in Fig.5. The energy gap values of Sb\(_2\)S\(_3\) thin

### Table 1. Crystallite size, dislocation density, micro strain and thickness of the prepared films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>Micro strain (x10^4)</th>
<th>Dislocation Density ((x10^{14}) lines/m(^2))</th>
<th>Thickness ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(_2)S(_3)</td>
<td>84</td>
<td>(6 \times 10^{-4})</td>
<td>1.417</td>
<td>15.3</td>
</tr>
<tr>
<td>(\text{Bi}_{0.1})((\text{Sb}_2\text{S}<em>3)</em>{0.9})</td>
<td>97</td>
<td>(3 \times 10^{-4})</td>
<td>1.0628</td>
<td>3.4</td>
</tr>
<tr>
<td>(\text{Bi}_{0.2})((\text{Sb}_2\text{S}<em>3)</em>{0.8})</td>
<td>129</td>
<td>(7 \times 10^{-4})</td>
<td>1.6866</td>
<td>4.1</td>
</tr>
<tr>
<td>(\text{Bi}_{0.3})((\text{Sb}_2\text{S}<em>3)</em>{0.7})</td>
<td>77</td>
<td>(3 \times 10^{-4})</td>
<td>0.6099</td>
<td>6.6</td>
</tr>
</tbody>
</table>
film is found to be $E_g = 1.60 \text{ eV}$ and $E_g = 1.55 \text{ eV} - 2.12 \text{ eV}$ for Bi doped Sb$_2$S$_3$ respectively. The lower band gap energy in Sb$_2$S$_3$ is due to smaller thickness and certain size effects like quantum size effect may arise in the film [18]. The result is in good agreement with the Sb$_2$S$_3$ thin films prepared by vacuum evaporation and chemical bath deposition methods [19, 20].

A consequence of quantization in the energy spectrum, the bottom of the conduction and top of the valence band may be separated by additional amount depending on thickness. The uppermost occupied valence band and lowest occupied conduction band are shifted to more negative and positive values respectively resulting in broaden of the band gap. The addition of Bi in Sb$_2$S$_3$ crystal lattice causes size differences. It may create new coordination and variation in the bonding and orbital contributions toward valence and conduction bands. Hence the addition of Bi introduces change in band gap.

Incorporation of Bi into Sb$_2$S$_3$ is confirmed using XRD and the structural changes reflected in UV –Vis and PL studies.

The photoluminescence technique has been widely used to investigate the energy levels of thin films. Fig.6 shows the photoluminescence spectra of Sb$_2$S$_3$ and Bi doped Sb$_2$S$_3$ thin films. The dominant sharp emission is noticed peak at 335 nm for all the films attributed to photon assisted transitions and electron-hole recombination after relaxation (band edge emission). This result is in close agreement with the report by F. Capezutto et al.[21]. The weak emission peak at 686 nm is due to the emission from the recombination of electrons and holes in trapped surface states located in the forbidden region of the band gap. The increase in photoluminescence intensity in 0.2% Bi is due to crystalline size because PL intensity is reciprocal of the square of the crystallite size [21]. All the emission are associate with defects emerging during the growth of crystallites and are related to deformation of crystallinity due to dislocations and large vacancies.

The dielectric constant is the result of the contribution of several kinds of polarizations as deformational (electronic, ionic) as well as relaxation (orientational and interfacial). When the frequency is increased, the electric dipoles cannot follow the field which leads to the decrease of orientation polarization. At high frequency, $\varepsilon$ reached a constant value due to interfacial polarization. Fig.7 shows the variation of capacitance with frequency for undoped Sb$_2$S$_3$ and 0. 1%, 0.2%, and 0.3% Bi doped Sb$_2$S$_3$ thin films in the frequency range 50 Hz to 5 MHz. The capacitance decreases with increasing frequency and attain a constant value at higher frequencies.

The variation of dielectric constant ($\varepsilon$) with frequency for the undoped Sb$_2$S$_3$ and 0. 1%, 0.2%, and 0.3% Bi doped Sb$_2$S$_3$ thin films is presented in Fig.8. The dielectric constant decreases with increasing frequency. This decrease may be due to fact the orientational polarization decreases when the frequency is increased. The value of dielectric constant attains a constant value at higher fre-
frequency due to interfacial polarization. The variation of real part of impedance ($Z'$) with the frequency for the of pure Sb$_2$S$_3$ and 0.1%, 0.2%, and 0.3% Bi doped Sb$_2$S$_3$ thin films is shown in fig.9. It is clear from the magnitude of $Z'$ decreases with the increase of frequency. This result is in agreement with the reported results published by N.Jessy Mathew et al., [7].

4. CONCLUSIONS

Sb$_2$S$_3$ and Bi-Sb$_2$S$_3$ thin films were successfully prepared by thermal evaporation technique. The deposited films were annealed at 250 °C and were characterized by using XRD, UV-Visible and Photoluminescence analysis. The XRD analysis confirms the orthorhombic structure of Sb$_2$S$_3$ thin films. The incorporation of Bi into the Sb$_2$S$_3$ lattice leads to prominent peak shift towards the lower angle. UV-Visible analysis shows Bi doped Sb$_2$S$_3$ thin films having higher optical absorption in the visible region than that of pure Sb$_2$S$_3$ thin films. 0.2% of Bi doped Sb$_2$S$_3$ thin film shows increased PL intensity compared to all other thin films due to the lower crystallite size. The value of capacitance, dielectric constant and real part of impedance decreases with increasing frequency for both the samples.

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REFERENCE

[16] N. Manjula, M. Pugalenthi, V.S. Nagarethinam, K. Usharani,


