Preparation and characterization of electrodeposited Bi$_2$S$_3$ thin films prepared from non-aqueous media

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Abstract

Semiconducting Bi$_2$S$_3$ thin films were prepared on stainless steel and fluorine-doped tin oxide (FTO) coated glass substrates from non-aqueous media using the electrodeposition technique. It has been found that bismuth nitrate and thiourea in the volumetric proportions as 8:2 and their equimolar solutions of 0.05 M concentration form good quality films of Bi$_2$S$_3$. The characterization of the prepared films was carried out using the X-ray diffraction and optical absorption techniques. These studies reveal that, as deposited films are polycrystalline having an optical band edge (direct) 1.8 eV. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Bi$_2$S$_3$ thin films; Electrodeposition; Polarization curves

1. Introduction

Despite of many potential, and actual, applications in photoelectronic, thermoelectric, photoelectrochemical devices, and solar selective and decorative coatings; group V–VI compounds are of continued interest for investigators from the preparative and characterization point of view, in order to test their suitability for a particular and desired application. Among these, Bi$_2$S$_3$ in thin-film form provides a promising candidate for photoelectrochemical (PEC) devices as its forbidden energy gap lies between 1.25 and 1.9 eV [1,2] which is appropriate for the conversion of solar energy into electrical energy.

Polyakov et al. [3] deposited Bi$_2$S$_3$ thin films on mica substrates by reactive vacuum deposition in sulfur vapor and observed an unusual structure which was accounted for the anisotropy of the sulfurization process. A similar method has been employed by Lukose and Pradeep [4] to obtain stoichiometric Bi$_2$S$_3$ thin films. ‘Electrodeposition’ of Bi$_2$S$_3$ films from acidic bath has been carried out using the three-electrode system under d.c. potentiostatic conditions onto stainless steel and fluorine-doped tin oxide (FTO) coated glass. The films prepared are also tested for the photoelectrochemical (PEC) effect using polysulfide as an electrolyte [5]. Yesugade et al. [6] have studied the structural and optical properties of electrodeposited Bi$_2$S$_3$, Sb$_2$S$_3$ and As$_2$S$_3$ thin films. Biswas et al. [7] prepared Bi$_2$S$_3$ thin films by using triethanolamine (TEA) and thioacetamide as a complexing reagent and sulfide ion source, respectively, for alkaline bath and Na$_2$S$_2$O$_3$ as sulfide ion source for acidic bath. Acharya et al. [8] chemically deposited amorphous Bi$_2$S$_3$ thin films and reported that annealing at 200°C does not influence the amorphous nature. Lokhande et al. [9–13] obtained amorphous Bi$_2$S$_3$ thin films from acidic as well as alkaline bath using disodium salt of ethylenedimethyltetra acetic acid (EDTA) as a complexing agent and Na$_2$S$_2$O$_3$, thiourea [CS(NH$_2$)$_2$], as a source of sulfide ions. The band gap energy was reported to be 1.5 and 1.74 eV. Non-aqueous chemical deposition of the films has also been reported [14] by dissolving Bi(NO$_3$)$_3$·5H$_2$O in acetic acid and thiourea in formaldehyde. The band gap energy reported to be 1.9 eV (direct). Deshmukh et al. [15] studied electrical and optical properties of the films obtained from aqueous alkaline bath using thiourea as a source of sulfur ions and TEA as a complexing reagent. The films are n-type, polycrystalline and having direct band gap of 1.7 eV. Pawar et al. [16] deposited Bi$_2$S$_3$ thin films by the spray pyrolysis technique and observed their electrochemical photovoltaic (ECPV) behavior.

The literature survey shows that all the Bi$_2$S$_3$ thin films deposited chemically from an aqueous medium are amorphous in nature. Recently, Killedar et al. [17] reported on nano-crystalline Bi$_2$S$_3$ thin films prepared from non-aqueous media by the spray pyrolysis technique.

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Among all the deposition techniques, electrodeposition is a simple, quick and economical method for the preparation of thin films. The growth rate can easily be controlled through electrical quantities, such as current density and deposition potential.

With a view to determining the effect of non-aqueous solvents on the crystallinity and other properties of electrodeposited Bi$_2$S$_3$ thin films, the films were deposited using a two-solvent system and their properties studied.

2. Experimental details

2.1. Preparation of thin films

Bi$_2$S$_3$ thin films were prepared on a conducting substrate, like stainless steel and fluorine-doped tin oxide (FTO) coated glass (area 0.4 × 2 cm$^2$) by the electrodeposition technique. The metallic substrate was mirror polished by fine, zero number polish paper and washed with labolene using distilled water. The back of the substrate was covered with an insulating tape. Conducting glass substrates were cleaned by 50% dilute HCl and then by doubly distilled water. The economical and inert, polished graphite plate (area 4 × 2 × 0.2 cm$^3$) was used as a counter electrode. The thin-film deposition was carried out from an unstirred solution at room temperature under potentiostatic mode. A three-electrode system was used and potentials applied were measured with respect to a standard calomel electrode (SCE). The distance between the anode and cathode was 0.4 cm.

Bismuth nitrate [Bi(NO$_3$)$_3$·5H$_2$O] was dissolved in acetic acid (glacial) and thiourea [CS(NH$_2$)$_2$] was dissolved in formaldehyde. The equimolar (0.1 m) solution with bath composition of bismuth nitrate and thiourea in volumetric proportions as 10:00, 09:01, 08:02, 07:03, 06:04, 05:05, 04:06, 03:07, 02:08, 01:09, 00:10 were used as electrolytes to determine the deposition potentials for stainless steel and FTO-coated glass substrates. The structural and optical studies of the films reveal that a good quality Bi$_2$S$_3$ thin-film formation occurs at 08:02 composition. By keeping the composition fixed, the equimolar concentration of the bath of Bi(NO$_3$)$_3$·5H$_2$O and CH$_2$(NH$_2$)$_2$ was varied from 0.025 to 0.1 M at intervals of 0.025 M. The deposition time and deposition potential were kept constant at 30 min and −0.220 V (SCE), respectively.

The as-deposited films were washed with doubly distilled water. The Bi$_2$S$_3$ thin films deposited on stainless steel substrate were dark gray in color, adherent to the substrate and uniform in appearance. The thickness of deposited thin film was determined by the weight difference method.

2.2. Characterization

The structural characterization of Bi$_2$S$_3$ thin films was carried out by analyzing the X-ray diffraction (XRD) patterns obtained using a Philips X-ray diffractometer model PW- 1710 (λ=1.5405 Å for CuKα radiation).

Optical absorption studies were carried out using a UV-visible-near-IR spectrophotometer (Hitachi model-330, Japan ) in the 350–850 nm wavelength range.

3. Results and discussion

The electrodeposition of Bi$_2$S$_3$ thin films has been carried out from a non-aqueous acidic solution containing bismuth and sulfur ions. The polarization curves were plotted to estimate the deposition potentials of Bi$_2$S$_3$ deposited onto the stainless steel (Fig. 1) and FTO coated glass substrates (Fig. 2) for the baths of various compositions. The estimated deposition potentials for Bi$_2$S$_3$ thin films on stainless steel and FTO coated glass substrate are given in Table 1. The deposition process begins as a result of the application of suitable potential.
Table 1

Estimated deposition potentials for Bi$_2$S$_3$ from polarization curves

<table>
<thead>
<tr>
<th>Bath composition Bi:S (pH=2)</th>
<th>Deposition potential vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stainless steel (mV)</td>
</tr>
<tr>
<td>0:10</td>
<td>−775</td>
</tr>
<tr>
<td>1:9</td>
<td>−625</td>
</tr>
<tr>
<td>2:8</td>
<td>−575</td>
</tr>
<tr>
<td>3:7</td>
<td>−550</td>
</tr>
<tr>
<td>4:6</td>
<td>−520</td>
</tr>
<tr>
<td>5:5</td>
<td>−460</td>
</tr>
<tr>
<td>6:4</td>
<td>−400</td>
</tr>
<tr>
<td>7:3</td>
<td>−300</td>
</tr>
<tr>
<td>8:2</td>
<td>−220</td>
</tr>
<tr>
<td>9:1</td>
<td>−</td>
</tr>
<tr>
<td>10:0</td>
<td>−</td>
</tr>
</tbody>
</table>

The thickness of the prepared films was determined by using the relation

\[ t = \frac{m}{\rho_s A} \]  

where \( m \) is the mass of the thin film deposited onto the substrate, \( A \) the area of the deposited thin film and \( \rho_s \) the density of the deposited material which is assumed to be same as that of the bulk material (\( \rho_s=6.80 \text{ gm cm}^{-3} \) for Bi$_2$S$_3$). The thickness of the film is of the order of 0.41 mm.

The XRD patterns of the films were recorded in the range of diffracting angles of \( 10^\circ < 2\theta < 70^\circ \). The XRD study reveals that Bi$_2$S$_3$ thin-film formation takes place at the composition and concentration of Bismuth nitrate and thiourea solution to be 8:2 and 0.05 M, respectively. The XRD patterns for as-deposited Bi$_2$S$_3$ thin films deposited at bath composition 8:2 and bath concentration 0.05 M on stainless steel and conducting glass substrates are shown in Figs. 3 and 4, respectively. These XRD patterns show the presence of [0 2 1] and [1 4 1] prominent planes of the Bi$_2$S$_3$ material. This shows that the thin films prepared from non-aqueous media are polycrystalline in nature. The standard and observed values of interplanar distance given in Table 2 (steel) and

Table 2

Comparison between standard (ASTM data card No. 17-3200) and observed \( d \) values for Bi$_2$S$_3$ thin films on stainless steel substrates

<table>
<thead>
<tr>
<th>Standard ( d ) (Å)</th>
<th>Observed ( d ) (Å)</th>
<th>( \beta \text{max} ) (%)</th>
<th>[h k l] plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.253</td>
<td>3.265</td>
<td>100</td>
<td>[0 2 1]</td>
</tr>
<tr>
<td>2.305</td>
<td>2.361</td>
<td>35.39</td>
<td>[0 4 1]</td>
</tr>
<tr>
<td>2.258</td>
<td>2.265</td>
<td>55.43</td>
<td>[1 4 1]</td>
</tr>
<tr>
<td>1.435</td>
<td>1.437</td>
<td>18.86</td>
<td>[5 2 2]</td>
</tr>
</tbody>
</table>

Table 3 (FTO glass) are in good agreement [18]. The material deposited is Bi$_2$S$_3$ as there is less probability of impurity compound deposition; the deposition of particular compound takes place at specific deposition potential [19,20].

By assuming orthorhombic structure of Bi$_2$S$_3$, the lattice parameters \( a_0 \), \( b_0 \) and \( c_0 \) are estimated and found to be \( a_0=10.84 \text{ Å} \) (standard \( a_0=11.49 \text{ Å} \)), \( b_0=11.38 \text{ Å} \) (standard \( b_0=11.30 \text{ Å} \)) and \( c_0=3.97 \text{ Å} \) (standard \( c_0=3.981 \text{ Å} \)). Hence, it is confirmed that the Bi$_2$S$_3$ structure is orthorhombic.

The variation of optical absorption at wavelength \( \lambda \) is shown in Fig. 5. From this, \( \alpha \) is found to be of the order of \( 10^4 \text{ cm}^{-1} \), indicating the presence of the direct band edge [21]. Following the normal theoretical analysis, the energy-dependent absorption coefficient \( \alpha(h\nu) \) can be expressed by the relation

\[ \alpha = \frac{\alpha_0(h\nu - E_g)^n}{h\nu} \]  

Table 3

Comparison between standard (ASTM data card No. 17-3200) and observed \( d \) values for Bi$_2$S$_3$ thin films on conducting glass substrates

<table>
<thead>
<tr>
<th>Standard ( d ) (Å)</th>
<th>Observed ( d ) (Å)</th>
<th>( \beta \text{max} ) (%)</th>
<th>[h k l] plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.253</td>
<td>3.258</td>
<td>100</td>
<td>[0 2 1]</td>
</tr>
<tr>
<td>2.258</td>
<td>2.259</td>
<td>27.83</td>
<td>[1 4 1]</td>
</tr>
<tr>
<td>1.857</td>
<td>1.857</td>
<td>10.42</td>
<td>[6 0 1]</td>
</tr>
<tr>
<td>1.606</td>
<td>1.631</td>
<td>11.46</td>
<td>[4 5 1]</td>
</tr>
</tbody>
</table>
Fig. 5. Plot of optical density ($\alpha$) vs. wavelength ($\lambda$) for Bi$_2$S$_3$ thin films.

Fig. 6. Plot of ($ahv)^2$ against $hv$ for Bi$_2$S$_3$ thin films.

for the allowed, direct and indirect transitions. For direct transitions, $n$ assumes the value 1/2, and for indirect transitions $n=2$. For large value of $\alpha$, corresponding to photon energies near band edge, a direct transition has been repeated for Bi$_2$S$_3$ single crystal [22,23].

In case of Bi$_2$S$_3$ thin films, many workers have explained the absorption on the basis of excitation [11]. Our measurements were carried out at room temperature; at this temperature, the excitation band is not likely to be present and the absorption is due to a band-to-band transition. This can be explained by plotting $(ahv)^2$ vs. $hv$ as shown in Fig. 6. The extrapolation of the plot to the energy axis gives a value of 1.8 eV as the band gap of Bi$_2$S$_3$ thin films. This value is in good agreement with the value reported earlier [17]. The higher band gap in the present case can be attributed to the interference by diffuse reflectance with polycrystalline deposits [23]. Bhattacharya and Pramanik [24] reported that the larger band gap might be due to a mixture of amorphous and crystalline phases and, further, that it is accounted for anisotropy of the film formation process.

4. Conclusions

A good quality Bi$_2$S$_3$ thin-film deposition using non-aqueous media is possible by the electrodeposition technique. As-deposited films are polycrystalline in nature. The optical band gap is 1.8 eV (direct).

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References