Electrical and optical properties of Bi$_2$S$_3$ thin films deposited by successive ionic layer adsorption and reaction (SILAR) method

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Abstract

Bi$_2$S$_3$ thin films were prepared on amorphous glass substrates by successive ionic layer adsorption and reaction (SILAR) method at room temperature using bismuth nitrate and thioacetamide as the cationic and anionic precursors in aqueous medium. The X-ray diffraction study reveals that as-deposited films of Bi$_2$S$_3$ are amorphous in nature, it becomes polycrystalline after annealing at 573 K. The decrease in activation energy from 0.65 to 0.36 eV and optical band gap energy, $E_g$, from 2.35 to 1.86 eV are observed as film thickness varies from 67 to 150 nm. Such changes are attributed to the quantum size effect in semiconducting films.

Keywords: Thin film; Electrical and optical properties

1. Introduction

Semiconductor thin films are always important in materials science due to their outstanding electrical and optical properties, which are useful in various optoelectronic devices. In this regard bismuth sulfide, Bi$_2$S$_3$, is one of such important materials whose band gap energy, 1.7 eV, lies in visible solar energy spectrum [1–3]. Various techniques have been employed for thin film deposition such as chemical deposition [4], interface gas solution [5], electrodeposition [6], and spray pyrolysis [7,8], etc. Like chemical bath deposition technique, the successive ionic layer adsorption and reaction (SILAR) technique for the preparation of thin films from aqueous solution is a promising technique because of its simplicity and economics. It is a relatively a new and less investigated method, first reported by Ristov [9] and the name SILAR was ascribed to this method by Nicolau [10–12]. In the last three decades, SILAR method has emerged as one of the versatile solution methods to deposit a variety of compound materials in thin film form. The SILAR method is based on the immersion of the substrate into separate anion and cation precursor solutions and rinsing between every immersion with ion-exchanged water to avoid homogeneous precipitation [13]. In chemical bath deposition method, the deposition of metal chalcogenide semiconductor thin films occurs when the substrate is immersed in a chemical bath containing the metal ions with suitable complexing agents and chalcogenide ions. In CBD all the precursors are present at the same time in the reaction bath and the reaction rate is controlled by slow release of ions from strong complexes. The film formation takes place when the ionic product exceeds the solubility product (IP > SP). This results in the formation of precipitate in the solution. Hence there is unavoidable wastage of material due to the formation of precipitate and control over process also was lost [14]. SILAR resembles in many ways chemical bath deposition. Both techniques utilize aqueous liquid and relatively uncomplicated apparatus. The basis of both techniques is the utilization of chemical forces between the ions in the liquid phase and the surface ions. In SILAR the facts affecting the process are the quality of the precursor solutions, their concentrations, pH values, complexing agents and individual rinsing and immersion time periods [15].

This paper reports the structural, optical, and electrical properties of SILAR prepared Bi$_2$S$_3$ thin films. The thickness of the film was varied by changing the number of SILAR deposition cycles and its effect on optical and electrical properties studied.
2. Experimental

The SILAR method is mainly based on the adsorption and reaction of the ions from the solution and rinsing between every immersion with deionised water to avoid homogeneous precipitation in the solution. The SILAR is based on sequential reaction at the substrate surface. The SILAR growth cycle contains four different steps: adsorption, rinsing, reaction and rinsing. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The adsorbed cations, \( pK^{aq\,+} \) and anion, \( a\, \text{A}\,^{\text{aq}\,-} \), are reacting to form solid compound \( \text{KpA} \), following the reaction

\[
(pK^{aq\,+} + q\,\text{X}_{aq\,+}^{\text{aq}}) + (b\,\text{Y}_{aq\,-}^{\text{aq}} + a\,\text{A}\,^{\text{aq}\,-}) \rightarrow \text{KpA} \downarrow \, + q\,\text{X}_{aq\,+}^{\text{aq}} + b\,\text{Y}_{aq\,-}^{\text{aq}} \tag{1}
\]

With \( ap = bq = b\,\text{q} \) where \( K \) represents cation (Cd\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\), Cu\(^{+}\), etc), \( p \) represents the number of cations, \( a \) represents the numerical value of charge on cation, \( \text{X} \) is a ion in cationic precursors having negative charge (Cl\(^{-}\), NO\(^{3-}\), etc.), \( q \) represents the number of \( \text{X} \) in cationic precursors and \( b \) the numerical value of charges on \( \text{X} \), \( b \) the number of \( \text{Y} \) in the anionic solutions, \( q \) the numerical value of charge on \( Y \) the ion which is attached to chalcogen ion, \( A \) represents the anion (O, S, Se and Te), \( a \) the number of anions. \( A \) is the chalcogen ion. In the presence of complexing agent, above reaction can be written as

\[
p(KC^[aq\,+] + q\,\text{X}^{aq\,+} + b\,\text{Y}^{aq\,-} + a\,\text{A}\,^{aq\,-}) \rightarrow Kp\,\text{A} \downarrow + q\,\text{X}^{aq\,+} + b\,\text{Y}^{aq\,-} \tag{2}
\]

where \( C \) is complexing agent.

The deposition of \( \text{Bi}_2\text{S}_3 \) thin films on glass slides at room temperature was achieved using 80 ml of 0.06 M bismuth nitrate as cationic and 100 ml of 0.07 M thioacetamide as anionic precursor solutions. The pH of thioacetamide solution was adjusted to 11 by adding ammonia in it. For the deposition process, a well-cleaned glass substrate was immersed in cationic precursor solution where \( \text{Bi}^{3+} \) ions were adsorbed on the substrate. After that the substrate was rinsed with ion-exchanged water to remove unadsorbed \( \text{Bi}^{3+} \) ions from the substrate. Further, the substrate was immersed into anionic precursor where \( \text{S}^{2-} \) ions diffuse from the solution in the diffusion layer towards the solid solution interface and reacts with \( \text{Bi}^{3+} \) to form \( \text{Bi}_2\text{S}_3 \). After this, rinsing again in ion exchange water to remove loose material from the substrate was followed. All these rinsing and immersion time periods were experimentally optimized to get good quality film.

The average thickness of the film was measured by the gravimetric and Fizzau’s method [16]. The two-point dc probe method of dark electrical resistivity was used to study the variation of resistivity with temperature. The structural studies were carried out using Philips PW 1710, diffractometer, with Cu K\( \alpha \) radiation having wavelength \( \lambda = 0.15405 \) nm. The optical characteristics were studied using Hitachi 330 spectrophotometer to find band gap energy. The microstructural studies were carried out using JSM-6360 (JEOL) scanning electron microscope.

3. Results and discussion

The SILAR is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The formation of \( \text{Bi}_2\text{S}_3 \) may involve following steps:

(1) The substrate was immersed into cationic precursor where \( \text{Bi}^{3+} \) ions get adsorbed on to the substrate surface.

\[
\text{Bi}_2(\text{NO}_3)_3 \cdot \text{H}_2\text{O} + \text{EDTA} \leftrightarrow [\text{Bi(EDTA)}]^{2+} + 5\text{H}_2\text{O} + \text{NO}_3^- \tag{3}
\]

(2) After rinsing in deionised water substrate was immersed into anionic precursor where \( \text{Bi}^{3+} \) ions react with \( \text{S}^{2-} \) to give \( \text{Bi}_2\text{S}_3 \), which can be explained by using tautomeric form of thioacetamide.

\[
\text{S} \quad \text{SH} \quad | \quad | \quad \text{CH}_3 - \text{C} - \text{NH}_2 \rightarrow \text{CH}_3 - \text{C} = \text{NH} \tag{5}
\]

In alkaline medium,

\[
\text{SH} \quad \text{OH} \quad | \quad | \quad \text{CH}_3 - \text{C} = \text{NH} + \text{OH}^- \rightarrow \text{CH}_3 - \text{C} = \text{NH} + \text{SH}^- \tag{6}
\]

\[
\text{SH}^- + \text{OH}^- \rightarrow \text{S}^{2-} + \text{H}_2\text{O} \tag{7}
\]

\[
2\text{Bi}^{3+} + 3\text{S}^{2-} \rightarrow 2\text{Bi}_2\text{S}_3 \downarrow \tag{8}
\]

The optimized conditions for deposition of \( \text{Bi}_2\text{S}_3 \) thin films are shown in Table 1. Using these conditions and by changing number of SILAR cycles the films having thickness 67–150 nm was prepared. As the films with number of SILAR deposition cycles less than 150 were discontinuous, number of cycles greater than 150 were taken. Fig. 1 shows variation of film thickness with number of SILAR deposition cycles. By definition SILAR consists of sequential saturated reactions whereby all the excess ions, i.e. loosely adsorbed ions, are rinsed away before the next reaction. Accordingly, the nominal film thickness per one SILAR cycle must be equal or lower than the lattice constant of the growing material. The average growth rate is 0.34 nm per cycle [11].

Structural identification of \( \text{Bi}_2\text{S}_3 \) films was carried out with X-ray diffraction in the range of angle 2\( \theta \) between 10\( ^\circ \) and 1000\( ^\circ \). Fig. 2 shows the XRD patterns of \( \text{Bi}_2\text{S}_3 \) thin films by
SILAR method, which were amorphous in nature. The observed broad hump in XRD pattern is due to amorphous glass substrate. The film having thickness 150 nm after annealing at 250 °C for 30 min becomes crystalline with orthorhombic structure. Table 2 summaries the crystallographic data of this film compared with ASTM X-ray powder data file (JCPDS 170320) [17]. These results are in good agreement with those obtained earlier by Benramdane et al. [18] and Mizoguchi et al. [19].

By applying Scherrer’s formula,

$$d = \frac{\lambda}{\beta \cos \theta}$$  \hspace{1cm} (9)

the average crystallite size of the annealed film was found to be 3 nm. Where \(\lambda\) is the wavelength used (0.154 nm); \(\beta\) is the angular line width at half maximum intensity in radians; \(\theta\) is the Bragg’s angle.

Table 2

<table>
<thead>
<tr>
<th>Bi₂S₃ film</th>
<th>Standard data</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°)</td>
<td>d (Å)</td>
</tr>
<tr>
<td>22.396</td>
<td>3.977</td>
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<tr>
<td>24.753</td>
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<td>2.248</td>
</tr>
<tr>
<td>46.708</td>
<td>1.944</td>
</tr>
</tbody>
</table>

Fig. 1. Variation of Bi₂S₃ film thickness with number of deposition cycles.

The dark electrical resistivity of Bi₂S₃ films was studied in the temperature range 303–480 °C using dc two-point probe method. Fig. 3 shows the variation of log of resistivity \((\log \rho)\) with reciprocal of temperature \((1/T) \times 10^3\). It is seen that resistivity decreases with temperature indicating semiconducting nature of films. The thermal activation energy was calculated using the relation,

$$\rho = \rho_0 \exp \left( \frac{E_0}{K T} \right)$$  \hspace{1cm} (10)

where \(\rho\) is resistivity at temperature \(T\), \(\rho_0\) is a constant, \(K\) is Boltzmann constant \((8.62 \times 10^{-5} \text{ eV K}^{-1})\) and \(E_0\) is the activation energy required for conduction. Fig. 4 shows variation in activation energy from 0.65 to 0.36 eV as thickness changes from 67 to 150 nm. Fig. 5 clearly shows variation in resistivity from 0.31 \(\times\) 10⁵ to 6.71 \(\times\) 10⁵ \(\Omega\) cm at temperature 333 K as thickness changes from 150 to 67 nm. These observations may be due to size effects that are arising because of quantum confinement of charge carriers within the particles. The high value of resistivity may be attributed due to nanocrystallinity of the film, grain boundary discontinuities, presence of surface states.
and small thickness of the film. Generally in semiconductors the conduction mechanism is highly influenced by the intercrystalline grain boundaries and strain fields associated dislocation network. The films with lower crystallites may have lower conductivity as compared to the films having larger crystallites. In the thermoemf measurements the polarities of the induced emf confirms n-type conductivity of the sample. Similar results were reported earlier by Gadakh et al. and Desai et al. [20,21].

The SEM of the Bi$_2$S$_3$ thin films of thickness 113 nm deposited on glass substrate was examined. The surface of the film is smooth and equally covered on the glass substrate (Fig. 6). It was observed from the micrograph study that the Bi$_2$S$_3$ film was homogeneous, without cracks or holes, and well adhered to the substrate.

The optical absorption of Bi$_2$S$_3$ thin films was studied in the wavelength range 300–850 nm and the variation of optical density ($\alpha t$) with wavelength ($\lambda$) is shown in Fig. 7. All the films show higher absorption on the shorter wavelength side with presence of an absorption edge. The nature of the transition (direct or indirect) is determined by using the relation

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$

(11)

where $h\nu$ is the photon energy, $E_g$ is the band gap energy, $A$ and $n$ are constants. For allowed direct transitions $n = 1/2$ for allowed indirect transitions $n = 2$. The plots of $(\alpha h\nu)^2$ versus $h\nu$ were shown in Fig. 8 for Bi$_2$S$_3$ films having different thicknesses. Since the variation of $(\alpha h\nu)^2$ with $h\nu$ for Bi$_2$S$_3$ films is a straight line indicating that the involved transition is direct one. Band gap energy, $E_g$ was determined by extrapolating the
Fig. 8. Plot of $(\alpha h)^2$ vs. $h\nu$ for Bi$_2$S$_3$ films with different thickness: A, 67 nm; B, 89 nm; D, 113 nm; E, 150 nm.

Fig. 9. Variation of optical band gap energy, $E_g$, with film thickness.

straight line portion to the energy axis for zero adsorption coefficient ($\alpha$). Fig. 9 shows variation in optical band gap energy from 1.86 to 2.35 eV with thickness from 67 to 150 nm. The thickness dependence of the band gap clearly indicates a blue shift with decreasing crystalline size, which is in good agreement with other reported results [4, 22–25]. The optical properties of the film were highly affected by the smaller grain size of the material [26]. The smaller the grain size the higher will be the light scattering [27]. Further, the optical band gap of semiconductors can be affected by the defects, charged impurities, disorder at the grain boundaries, stoichiometry as well as the three-dimensional quantum size effects, which could increase the energy band gap with the decrease of particle size. In this study, the variation of the band gap was represented as a function of the film thickness. $E_g$ of the bulk Bi$_2$S$_3$ crystals ($\sim$1.5 eV) is smaller than the thickest 150 nm film. It may be due to the fact that the energy band gap of a semiconductor is affected by the residual strain in the film on the substrate.

4. Conclusions

Growth of Bi$_2$S$_3$ thin films at low temperature by a simple chemical method, SILAR is possible. XRD studies reveal that as-deposited Bi$_2$S$_3$ films are amorphous and exhibit nanocrystalline structure after annealing at 573 K. Optical studies show that the absorption spectrum is due to transition from one band to another and is mainly caused by allowed direct transitions. The optical band gap energy varies from 1.86 to 2.35 eV with thickness variation from 67 to 150 nm. Variation of band gap with grain size reveals quantum size effect. The electrical resistivity and therefore activation energy are observed to be thickness-dependent.

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