CHAPTER V

GROWTH AND CHARACTERIZATION OF Bi$_2$S$_3$ THIN FILMS

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5.1 INTRODUCTION

Nanocrystalline semiconductors are of great interest for scientific research due to their important applications in advanced electronic and optoelectronic devices. Semiconducting bismuth sulfide thin film has been receiving considerable attention in recent years because of its applications in various fields of science and technology [1]. Bi$_2$S$_3$ is one of the important materials whose band gap energy 1.7 eV lies in visible solar energy spectrum which makes it useful for solar energy conversion devices [2]. Bi$_2$S$_3$ belongs to the members of the V-VI group of compound semiconductors which are technically important materials in view potential applications in thermoelectric conversion, optoelectronic devices and IR spectroscopy and excellent properties like photosensitivity, photoconductivity, solar cell[3,4]. Bi$_2$S$_3$ thin film is a particularly challenging material because of its midway band gap (1.25-1.7 eV), reasonable conversion efficiency and stability together with low cost [5]. Thus it is an ideal candidate for solar cell and photodetector in the visible wavelength region. Due to significant thermoelectric effect, this material is important in thermoelectric applications. Various reports are available for deposition of Bi$_2$S$_3$ thin film by different methods such as chemical bath deposition [1,6-8], spray pyrolysis [9-11], solution-gas interface technique [12], electrode position [13,14] using different sulphide ions releasing source such as thiosulfate, thioactamide and thiourea [15-17]. But very few reports are available on deposition of Bi$_2$S$_3$ thin film by successive ionic layer adsorption and reaction method (SILAR) [2,18,19].

In chemical bath deposition, film formation on substrate takes place when ionic product exceeds the solubility product. It results into precipitate formation, to avoid the unnecessary precipitation chemical method is modified known as successive ionic layer adsorption and reaction (SILAR) method. The SILAR method for preparation of thin
film is attractive, easy to control the overall growth rate, cost effective, less time consuming compared to other methods [20]. It is based of immersion of substrate in separately placed cationic and anionic precursors and rinsing between every immersion with ion exchange water to avoid homogeneous perception [21]. It depends on attractive force between the ions and surface of the substrate. The ad-atoms holding on surface of the substrate may be due to the residual force.

In the present chapter preparation, characterization and measurement of structural, optical and electrical properties are reported for Bi$_2$S$_3$ thin film deposited by SILAR method. The preparative parameters such as concentration of precursor’s solutions, immersion time, rinsing time, number of deposition cycles, etc. are optimized.

5.2 EXPERIMENTAL DETAILS

The successive ionic layer adsorption and reaction (SILAR) method mainly based of immersion of the substrate into separate cation (Bi) and anion (S) precursor solutions and rinsing between every immersion with ion-exchange water to avoid homogeneous precipitation. Fig. 5.1 shows schematic representation for the deposition of Bi$_2$S$_3$ thin film by SILAR technique.
Fig. 5.1 The scheme of SILAR method for the deposition of Bi$_2$S$_3$ thin films

1) Cationic precursor [Bismuth nitrate solution]  2) Ion-exchange water
3) Anionic precursor [Thioacetamide solution]  4) Ion-exchange water.

5.2.1 Substrate Cleaning

Substrate cleaning is one of the most important steps for obtaining the reproducible properties of the films. It also affects the stiochiometry, adhesion, smoothness, and uniformity of the film. The glass microslides supplied by ‘Blue Star’ of the dimensions 7.8 cm x 2.22 cm x 0.1 cm have been used as the substrates. The following procedure was adopted for cleaning the glass substrates.

a) Substrates were boiled in chromic acid for five minutes and were washed with deionized water.

b) Substrates were dipped in ‘labolean’ detergent solution and again washed with deionized water.

c) Substrates were cleaned with ultrasonic cleaner for five minutes.

5.2.2 Preparation of Solution

Chemicals used for preparing Bi$_2$S$_3$ films were as follows Bismuth nitrate (AR grade), thioacetamide (AR grade), triethanolamine and hydrazine hydrate. All chemicals were
supplied by Loba Chemie, Mumbai. All solutions were prepared in double distilled water.

5.2.3 Sample Preparation

For the deposition of Bi$_2$S$_3$ thin films, the cationic precursor 0.003 M aqueous solution of bismuth nitrate [Bi(NO$_3$)] with pH ~9 was used. Triethanolamine (TEA) is used as complexing agent in the cationic precursor. The anionic precursor was 0.004 M of thioacetamide [CH$_3$-CS-NH$_2$] with pH ~11 [22]. The pH of the anionic precursor was adjusted with the addition of hydrazine hydrate. A well-cleaned glass substrate was immersed in cationic precursor solution of bismuth nitrate for 20 s [Fig. 5.1] in which Bi$^{3+}$ ions are adsorbed on the surface of the substrate. The substrate was rinsed with ion exchange water for 40 s, to remove unadsorbed ions. The substrate was then immersed in an anionic precursor of thioacetamide solution for 20 s, in which S$^{2-}$ ions are reacted with adsorbed Bi$^{3+}$ ions on the glass substrate. This was followed by rinsing again in ion exchange water for 40 s, to remove unreacted S$^{2-}$ ions. This completes one cycle for the deposition of Bi$_2$S$_3$ thin films. By repeating such cycles for 20 times, continuous Bi$_2$S$_3$ film on glass substrate was obtained. The deposition was carried out at room temperature (27$^\circ$C).

5.2.4 Characterization of Bi$_2$S$_3$ Thin Films

The Bi$_2$S$_3$ films prepared at optimized preparative parameters were characterized by using following techniques.

5.2.4.1 Films Thickness

Film thickness measurement of Bi$_2$S$_3$ thin films was carried out by gravimetric weight difference method.
5.2.4.2 X-ray diffraction

XRD studies were carried out using Bruker AXS-Germany model no. D8 Advance diffractometer, with CuKα radiation (λ=1.540Å).

5.2.4.3 Scanning Electron Microscopy

The surface morphology of Bi₂S₃ thin film was studied by using scanning electron microscopy (SEM) (Model: JEOL JSM –5600).

5.2.4.4 Atomic Force Microscopy

Atomic force microscope digital unit was preferred for surface morphology and roughness analysis of the film in the form of two dimensional views.

5.2.4.5 Optical Absorption

The variation of absorbance ‘αt’ with wavelength ‘λ’ for all films has been carried out with UV-Vis (Perkin Elmer, Lambda-25) spectrophotometer, in the wavelength range 400-1100 nm. The data were further analyzed for the estimation of the bandgap energy of the CdS-Bi₂S₃ film material.

5.2.4.6 Electrical Resistivity

The two point d.c. probe method was used to study the variation of resistivity with temperature.

5.2.4.7 Thermoemf

The thermoelectric properties of Bi₂S₃ thin film studied by thermoelectric measurement unit.

5.2.4.8 I-V Measurements

The room temperature resistivity measurement was performed with I-V characteristics unit (Lab equipment unit model no. 2004 interfaced with computer), the voltage applied over the range ± 0.5V. Silver paste was employed to ensure good ohmic contacts with
the films. I-V measurements were made between the top and the back contacts made to film using I-V measurement system interfaced with computer.

5.3 RESULTS AND DISCUSSION

5.3.1 Optimization of Preparative Parameters

By making several trials for different concentrations, immersion cycles and immersion time preparative conditions are optimized as shown in Table 5.1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cationic Precursors</th>
<th>Anionic Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bismuth Nitrate [Bi (NO₃)₃]</td>
<td>Thioacetamide [CH₃-CS-NH₂]</td>
</tr>
<tr>
<td>Concentration (M)</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>PH</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Immersion cycles</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Immersion time (S)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Rinsing time (S)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Deposition temp (°C)</td>
<td>27</td>
<td>27</td>
</tr>
</tbody>
</table>

In the present study, for the optimization of bismuth ions equal volumes of cationic precursor solution (bismuth nitrate) and anionic precursor solution (sodium sulphide) were taken into two beakers. The pH of the anionic precursor was maintained by dropwise addition of hydrazine hydrate. Triethanolamine (TEA) is used as complexing agent in cationic precursor. By keeping number of immersions cycles as 20, immersion time 20 s, and rinsing time 40 s constant, the concentration of cationic precursor solution was varied from 0.001 to 0.005 M, and respective Bi₂S₃ thickness was measured.
Fig. 5.2 (a) Plot of Bi$_2$S$_3$ thin film thickness as a function of concentration (M).

Fig. 5.2 (a) shows variation of film thickness against concentration of bismuth nitrate. The Bi$_2$S$_3$ film formation starts from concentration 0.001 M of bismuth nitrate, when ionic product exceeds the solubility product and reaches maximum film thickness value at concentration of 0.03 M, after which Bi$_2$S$_3$ thin film thickness goes on decreasing which may be due to the formation of outer porous layer as discussed by Desai et. al.[17].

Fig. 5.2 (b) Plot of variation of Bi$_2$S$_3$ thin film thickness with immersion cycles.
Fig. 5.2 (b) shows the variation of film thickness with number of immersion cycles for optimized concentration of bismuth nitrate (0.003 M) and thioacetamide (0.004 M). The film has maximum thickness of 0.65 µm at 20 immersion cycles. Afterwards, the film thickness decreases due to peeling off the outer powdery layer.

![Graph showing film thickness variation with immersion time](image)

Fig. 5.2 (c) Plot of Bi$_2$S$_3$ thin film thickness as a function of immersion time (s).

Fig. 5.2(c) shows Bi$_2$S$_3$ thin film thickness variation with immersion time for optimized values of concentration and number of immersion cycles. From this graph, it was concluded that Bi$_2$S$_3$ thin films with maximum terminal thickness of 0.65 µm could be deposited with SILAR technique.

### 5.3.2 Reaction mechanism

Bi$_2$S$_3$ thin films were carried out by successive ionic layer adsorption and reaction (SILAR) method [18]. The SILAR method is based on sequential reaction at the substrate surface. The growth mechanism of Bi$_2$S$_3$ thin films involves following steps.
Fig. 5.3 Reaction mechanism of Bi$_2$S$_3$ thin film

(1) Bismuth nitrate used as the cationic precursor was 0.003 M in concentration with pH~ 11. When the substrate was immersed in cationic precursors Bi$^{3+}$ ions are adsorbed on the surface. It was rinsed in ion exchange water for 40 s, to avoid the excess of ions

$$[Bi(TEA)^{3+}] \rightarrow Bi^{3+} + TEA \ldots \ldots \ldots \ldots \ldots (5.1)$$

(2) The anionic precursor used as thioactamide of concentration 0.004 M with pH ~11. The anionic precursor solution the hydrolysis of thioacetamide takes place, which releases sulphide ions as

$$ S \quad SH$$

$$| \quad |$$

$$CH_3 - C - NH_2 \rightarrow CH_3 - C = NH \ldots \ldots \ldots \ldots \ldots (5.2)$$

$$SH \quad OH$$

$$| \quad |$$

$$CH_3 - C = NH + OH \Rightarrow CH_3 - C = NH + SH^- \ldots \ldots \ldots \ldots \ldots (5.3)$$

$$SH + OH^- = S^{2-} + H_2O \ldots \ldots \ldots \ldots \ldots (5.4)$$
(3) After immersion of substrate in \( S^{2-} \) ions containing solution, the \( S^{2-} \) reacts with preadsorbed \( Bi^{3+} \) to form a layer of \( Bi_2S_3 \) thin film. It rinsed in ion exchange water for 40 s, to avoid the excess of ions.

\[
2Bi^{3+} + 3S^{2-} \rightarrow Bi_2S_3 \text{......... ........... ..}(5.5)
\]

Thus one SILAR cycles of \( Bi_2S_3 \) thin film was completed, 20 such deposition cycles were repeated at room temperature. After 20 deposition cycles a slight decrease in \( Bi_2S_3 \) thin film thickness was observed, this is possibly due to formation of an outer porous \( Bi_2S_3 \) layer. The obtained \( Bi_2S_3 \) thin film was annealed up to half hour at 250°C.

5.3.3 X-ray diffraction (XRD) studies

The XRD patterns of as deposited and annealed \( Bi_2S_3 \) thin films were studied by X-ray diffractometer with CuK\( \alpha \) radiation. The observed plane orientations of as deposited \( Bi_2S_3 \) thin film show \( (1 0 2) \), \( (1 2 1) \), \( (0 5 2) \) as shown in Fig. 5.4 and annealed \( Bi_2S_3 \) thin film orientations is \( (0 0 2) \), \( (0 1 3) \), \( (1 4 2) \), \( (2 0 4) \) confirmed orthorhombic phase of \( Bi_2S_3 \) as shown in Fig. 5.5. The low intensity and broad diffraction peak suggest that the as-deposited thin film is amorphous in nature. After annealing the film shows sharp peaks, its intensity increases and crystanity of the sample also increases. This is in good agreement with the results reported by Yesugade et. al. [23]. \( Bi_2S_3 \) thin film is found to orthorhombic structure by comparing observed “d” value, with standard “d” value from JCPDS card no. (84-0279) [24].
Fig. 5.4 and 5.5 XRD patterns of as deposited and annealed Bi$_2$S$_3$ thin films.

The calculated d values of Bi$_2$S$_3$ thin films are in good agreement with standard value. The lattice parameters were calculated using the relation.

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \] \hspace{1cm} (5.7)

Calculated values of lattice parameters are \( a = 3.98 \) Å, \( b = 11.16 \) Å and \( c = 11.30 \) Å were in well agreement with the standard values of orthorhombic structure of Bi$_2$S$_3$ material [25].

Crystallite size has been calculated by using Scherer’s formula

\[ D = \frac{K\lambda}{\beta \cos \theta} \] \hspace{1cm} (5.8)

Where the constant \( K \) is a shape factor usually 0.94, \( \lambda \) is the wave length of X-ray (\( \lambda = 1.540 \)Å), \( \beta \) is the FWHM in radians and \( \theta \) is the Bragg’s angle. Crystallite size found
to increase from 5 nm to 12 nm for as-deposited and annealed Bi$_2$S$_3$ thin films, respectively due to removal of defect levels.

### 5.3.4 Surface morphology study

Scanning electron microscopy is helpful to study the surface morphology of thin film. Fig. 5.6 (a) (b) show SEM images of as deposited and annealed Bi$_2$S$_3$ thin films respectively. The SEM results indicate the smoothness of film surface which is homogenous and without any cracks; Bi$_2$S$_3$ is equally covered on glass substrate posses amorphous phase. After annealing improvement in crystallinity is observed.

![SEM micrographs of Bi$_2$S$_3$ thin films on glass substrate](image)

Fig. 5.6  SEM micrographs of Bi$_2$S$_3$ thin films on glass substrate

(a) as-deposited (b) annealed at 250 °C in air.

### 5.3.5 Atomic Force Microscopy

Fig. 5.7 (a) (b) shows two-dimensional (2-D) images of as-deposited and annealed Bi$_2$S$_3$ thin films, respectively. Atomic Force Microscopy is helpful to study surface roughnesses of
the films. The Fig. 5.7 (a) confirms that the deposited Bi₂S₃ thin film shows uneven, irregular shape and size grains distributed over the substrate, while on annealing treatment the modifications are observed in the form of grain agglomeration and improvement in the shape and size is as shown in Fig. 5.7 (b). From these observations, it is evident that the annealing could improve the crystallinity and quality of the thin films.

![Fig. 5.7 AFM of Bi₂S₃ thin films (a) as deposited (b) annealed at 250°C in air.](image)

5.3.6 Optical Absorption

UV-Vis spectroscopy has become an effective tool in determining the size and optical properties of the nanoparticles. The optical absorbance \( (\alpha t) \) spectra of as-deposited and annealed Bi₂S₃ thin films, are recorded in the wavelength range of 400-1100 nm. The absorption spectra of as-deposited and annealed Bi₂S₃ thin films were studied.

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

(5.9)
Where $E_g$ is the separation between the valence and conduction bands, and $n$ is a constant equal to $1/2$ for direct gap materials and $2$ for indirect gap materials. The plot of $(\alpha h\nu)^2$ against $h\nu$ is linear, then the transition is direct allowed [11].

![Graph showing absorption vs wavelength](image)

**Fig. 5.8** Plot of absorption ($\alpha t$) Vs wavelength ($\lambda$) for thin film

Figure 5.9(a) shows the plot of $(\alpha h\nu)^2$ vs $h\nu$ to derive the energy band gap of the as deposited and annealed Bi$_2$S$_3$ thin films which is calculated by using absorption spectra. The energy band gap for as deposited and annealed thin films were calculated using the following equation.

$$(\alpha h\nu)^2 = \beta^2(h\nu - E_g) \quad \text{...............5.10}$$

Where $\alpha$ is absorption coefficient, $\beta$ is constant, $E_g$ is band gap energy. The band gap energy decreases from 1.69 to 1.62 eV for as deposited and annealed Bi$_2$S$_3$ thin films respectively, which are in good agreement with reported values[10]. The observed decrease in energy band gap can be attributed to the improved crystallites size of the material when compared to the as deposited Bi$_2$S$_3$ thin films [26,27]. The molecular band gap of Bi$_2$S$_3$ thin film as shown in Fig. 5.9(b) in the form of homo lumo.
Growth, structural and optoelectronic properties of CdS-Bi$_2$S$_3$ semiconductor thin film for photosensor applications.

Fig. 5.9 (a) Plot of $(\alpha h \nu)^2$ Vs $h \nu$ for Bi$_2$S$_3$ thin films.

Fig. 5.9 (b) Band gap variation of Bi$_2$S$_3$ thin film

5.3.7 Electrical Resistivity

Fig. 5.10 shows the plot of Log $\rho$ verses 1000/T to characterize the nature of the thin film. This characterization was carried at room temperature using two-point probe dc measurement method. From Fig. 5.10 it is observed that the resistivity has inverse relation with the applied temperature, which confirms the semiconducting behavior of thin film. The high resistivity is observed for as deposited thin film which may be due to presence of surface state and grain boundary discontinuations; while on annealing...
A decrease in resistivity is observed; this may possibly be related to increased charge carrier mobility in lower energy band gap material.

The activation energy is estimated from the slope of the Log (ρ) versus 1/T and determined using the following equation [24]:

\[ \rho = \rho_0 \exp (E_a / KT) \] (5.11)

Where, \( \rho \): resistivity at temperature T, \( \rho_0 \): a constant, k: Boltzmann constant and \( E_a \): the activation energy.

![Fig. 5.10 Plot of Log ρ Vs 1000/T for Bi₂S₃ thin film.](image)

Activation energy for as deposited and annealed Bi₂S₃ thin films was found to be 0.006 eV and 0.005 eV respectively [24]. The decrease in activation energy is mainly attributed to the increased density of defect states in the annealed thin film [26].

5.3.8 Thermoemf

Fig. 5.11 shows thermoemf measurements of annealed and as-deposited Bi₂S₃ thin films. The temperature difference between ends of the sample causes transport of the carriers from the hot to the cold end and creates an electric field which gives rise to the
thermal voltage; this thermally generated voltage is directly proportional to the temperature difference across the ends of the semiconductor [28].

Fig. 5.11 Plot of thermoemf (ΔV) against temp. difference (ΔT) for Bi₂S₃ thin films.

From thermoemf measurement, it is found that the polarity of thin film is positive towards the hot end, indicating the Bi₂S₃ is n-type semiconductors. The negative sign of the TEP suggests that the major contribution to the conductivity is due to the electrons. The plot shows that the improvements of both electrical conductivity and seeback coefficient can be realized by increasing carrier mobility [29]. The thermoemf in annealed film is higher than which may be due to increase in crystallite size and density of defect levels [26].

The electron density was calculated by using the relation [11]

\[
\text{Log} (n) = \left( \frac{3}{2} \right) \text{log}(T) - 0.005 \text{TEP} + 15.719 \quad \text{......... \text{(5.12)}}
\]

The electron density is of the order of \(10^{19}\) cm\(^{-3}\), charge carrier mobility \(\mu\) is determined from the relation

\[
\mu = \delta / \eta e \quad \text{.................(5.13)}
\]

Where \(n\) is electron density and \(\delta\) is the conductivity.
The variation of log ($\mu$) (left y axis) versus 1000/T and variation in log $\eta$ (right y axis) versus 1000/T is as shown in Fig. 5.12. The intergranular barrier height ($\Phi_b$) were calculated from the following equation

$$\mu = \mu_0 \exp \left( -\frac{\Phi_b}{KT} \right) \ldots \ldots (5.14)$$

The value of $\Phi_b$ obtained from the plot of log ($\mu$) vs 1/T is 0.3051 eV and 0.058 eV for as deposited and annealed film respectively [30].

Fig. 5.12 Variation of Bi$_2$S$_3$ thin film. log($\mu$) and log $\eta$ versus 1000/T for

(a) as deposited (b) annealed at 250$^\circ$C in air.

5.3.9 I-V Measurement
Fig. 5.13 shows I-V characteristics of as deposited and annealed Bi$_2$S$_3$ thin film under dark and on illumination with light (100W). The photo generated charge carriers were found to increase with the increasing power. The excitation of valence electrons into the conduction band significantly improves the electrical conductivity of the semiconductors; this phenomenon is known as simply photoconductivity. Increase in the intensity increases causes increase in the number of intrinsic carriers (electrons and holes) by several orders of magnitude [25]. Since photoconduction increases the intrinsic carrier concentration (electrons and holes), the resistance decreases with increasing power. Therefore, observing the variation in the I-V plots with respect to the intensity with which the optimized samples were illuminated suggests that Bi$_2$S$_3$ film exhibits photoconductivity phenomena useful in photosensor applications.

![I-V Characteristics of Bi$_2$S$_3$ Thin Films](image)

**Fig. 7.9** I-V characteristics of Bi$_2$S$_3$ thin films.

Its photosensitivity[31,32] were calculated by the equation.

\[
S = \frac{R_d - R_l}{R_d} 
\]  

Where $R_d$ and $R_l$ is the resistance in dark and under light, respectively.
Fig. 5.14 shows the plot of photosensitivity verses intensity of light obtained when the Bi$_2$S$_3$ thin film exposed to different sources of lights such as 40 W, 60 W and 100 W. It is clear from the figure that the charge carrier density increase with increase in light intensity and consequently the photosensitivity also increases. The photosensitivity is observed to be higher in annealed thin film i.e. 61% as compared to as-deposited thin film which is 54% When the film was exposed to the source of light is 100 W the current is increased.

![Plot of photosensitivity verses intensity of light](image)

**Fig. 5.14** Plot of photosensitivity verses intensity of light.
Fig. 5.15 Plot of current response of Bi$_2$S$_3$ thin films as a function of exposure time.

Another important parameter to evaluate photocurrent response. Fig. 5.15 represents the current response as a function of exposure time. From the figure it confirms that for long term exposure the current in the thin film increases which may be related to generation of more number of free charge carriers. The drastic effect of air annealing on the photocurrent response of bismuth sulphide samples is shown in Fig. 5.15. Further illumination and annealing enhances photoresponse and maximum photocurrent is obtained.
REFERENCES


