Experimental Techniques for Deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) Doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$

Mixed Metal Chalcogenide Thin Films

4.1 Introduction

The thermoelectric device can convert thermal energy from a temperature gradient into electric energy. When a temperature differential is established between the hot and cold ends of the semiconductor materials, a voltage is generated. The thermoelectric devices can also act as power generators. Oppositely, thermoelectric devices can convert electrical energy into a temperature gradient. Thermoelectric devices have several advantages over traditional coolers and power generators such as no moving parts, no working fluid (e.g. steam or Freon substitutes) and noiseless operation [1]. Metal chalcogenide plays important role as a thermoelectric material. Among all the chalcogens Te and Se is one of the most important chalcogen elements. The works on binary Se-alloys have already been reported [2-6]. Se-Te has been used as a base material and incorporation of Bi as a third element has been studied [7]. A large value of the thermoelectric efficiency $Z$ of these materials is due to the high degeneracy of the energy band edges. It is necessary to increase the Seebeck coefficient or the electric conductivity in order to increase the thermoelectric efficiency. This is of particular interest for applications at room temperature. Now a day Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ is the best performing n-type thermoelectric material [8-12].

At present, thin film solar cells are the most interesting scheme in the solar cell development and research. Binary chalcogenide material has special applications in intercalation superconductors photo electrochemical cell. The search for new semiconducting material for solar energy conversion has been the subject of intensive research. Therefore Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films are the most promising material for thin film solar cells. It has many advantages such as low cost production, high efficiency and long term stability. The main approach of electrochemical photovoltaic cell (ECPV) is cell of trapping the solar energy is the intensive research area become of its economic viability.
and processing simplicity. The present work, we have studied the structural and electrical properties of ternary Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb(III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films.

4.2 Experimental set up for deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films

Experimental set up for deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films is as below

4.2.1 Deposition Chamber

A thin film deposition chamber was designed and fabricated in our laboratory having dimensions 1.8 x 0.8 x 1 m$^3$ to maintain clean ambient atmosphere necessary for the deposition and to protect the deposition system from the physical hazards. In this topic we deal with fabrication of the thin film deposition technique and associated accessories. It consist of constant speed motor, metallic stand, substrate holder, temperature controller, reaction container, constant temperature bath etc. At the top of the deposition chamber it is provided with an exhaust fan to expel toxic gases. Diagrammantic representation of thin film deposition chamber, deposition assembly and its cross sectional view is shown in Figure 4.1 and 4.2 respectively.
4.2.2 Substrate holder

In order to having proper bulk mixing of the solution in the reaction container was depending upon substrate holder. Substrate holder having thickness 1 cm with four slots having diameter 5 cm with 4 slots cut into the disc in such a way that the rotating substrates did not touch the wall of the solution container. It is fabricated in our laboratory by using Bakelite material. Geometry of substrate holder plays important role in quality and uniformity of the thin film prepared by arrested precipitation technique. This substrate holder used for holding the substrate in horizontal position as shown in Figure 3.3. Position of the motor was adjusted to a drilling machine stand in such a way that more than 2/3 portion of the substrates will dip into the solution container and substrates are exactly perpendicular to each other. The substrates to be deposited were fitted in these slots with the help of screws in such a way that rotating substrates do not touch the wall of the solution container.

4.2.3 Temperature bath

The constant temperature bath was prepared in our laboratory with dimension 3.5” x 6” having temperature controller attachment. Then it is agitated using Remi-magnetic stirrer. In order to maintain uniform deposition
temperature, paraffin oil was kept in a bath. Height of the bath was adjusted to a required level by movable stand.

4.2.4 *Constant speed motor*

Speed motor is a single–phase a. c. gear motor type [ Remi Make Universal RU-56-24.1/8 HP (1.1 Amp)]. The speed of motor can be varied from 30 rpm to 150 rpm with the help of regulator. A dimmer stat cum regulator was also provided to control speed of motor. The motor is fitted to a sturdy metallic stand. A metallic rotating shaft having length 15 cm and diameter 0.5 cm was attached to the motor. One end of the rod was attached to a constant speed a. c. gear motor while other end was fitted to a substrate holder as shown in Figure 4.3 A & 4.3 B.

![Figure 4.3. A) Design of the substrate holder, B) Cross sectional view of substrate holder](image)

4.2.5 *Substrate cleaning*

Glass slides of dimensions 75 mm x 25 mm x 1.35 mm were used as substrates. In order to get good adhesion between the chemically deposited films and the substrates, a special attention was paid to the pre treatment of the substrates. So in chemical bath deposition, substrate cleaning plays an important role because the cleanness is a measure of sticking of the film to
the substrate support. Cleanness is the process of breaking the bonds between substrates and contaminants (e.g. adsorbed water, grease and airborne dust and oil particles) without damaging the substrates. In our study the glass substrate and fluorine doped tin oxide (F:SnO₂) coated glass substrates were used for deposition of thin films. The conducting FTO coatings were prepared using pent hydrated stannic chloride (SnCl₄·5H₂O) (purity 98%) and ammonium fluoride (NH₄F) (purity 95%) as precursor salts. The solution was prepared in double distilled water. The FTO coated conducting glass substrates with 90–95% transparency and sheet resistance of 10–15 Ω/cm² were obtained at 500°C. These FTO-coated glass substrates were further used as conducting substrates for the deposition of ternary Bi₂(Te₁₋ₓSeₓ)₃ and Sb (III) doped Bi₂(Te₁₋ₓSeₓ)₃ mixed metal chalcogenide thin films by Arrested precipitation technique.

The glass substrate and fluorine doped tin oxide (F:SnO₂) coated glass substrates are cleaned using following procedure:

i) The glass substrate and the fluorine doped tin oxide (F:SnO₂) coated glass substrates were washed with detergent solution and then with distilled water.

ii) The glass substrates were boiled in chromic acid for 20 minutes and rinsed with double distilled water.

iii) At last substrates were cleaned with Acetone and dried.

iv) Thoroughly cleaned glass substrates were mounted on a substrate holder.

4.3 Deposition of Bi₂(Te₁₋ₓSeₓ)₃ and Sb(III) doped Bi₂(Te₁₋ₓSeₓ)₃ thin films by Arrested precipitation technique

In chapter two we discussed different techniques for deposition of the various metals, ceramic polymer and alloy thin film on variety of the substrate materials. Out of these in our research we use Arrested precipitation technique (APT) for deposition of ternary Bi₂(Te₁₋ₓSeₓ)₃ and Sb (III) doped Bi₂(Te₁₋ₓSeₓ)₃ mixed metal thin films. Because a deposition technique depends upon several factors such as film thickness, surface area, nature of substrate supports application of thin film. This process is relatively slow therefore it facilities better orientation, crystallinity of thin film. Also this method is low
deposition process it avoids intermetallic conversion as well as thermal expansion of substrate. APT is important not only for effectiveness in the reduction of low cost. But also for the high quality of the materials one can achieves by such method.

In the arrested precipitation method we use organic complexing agent such as EDTA, citric acid, triethanolamine, tartaric acid etc. to arrest the metal ions by forming metal ligand complex. So controlled dissociation of arrested metal ion at basic pH was takes place slowly (ion by ion). The film formation involves creation of a nucleation centres at the substrate surface followed by growth of metal chalcogenide by the ion by ion condensation of appropriate ions from solutions. Certain time this result in saturation of film growth known as terminal growth phase of thin film deposition [13-15].

4.3.1 Solutions required for preparing Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ and Sb(III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$

All chemicals used in experiment were analytical reagent (AR) grade manufactured by E-Merck and Hi-Media. These chemicals are

- Bismuth nitrate \( \text{Bi(NO}_3\text{)}_3.5\text{H}_2\text{O} \)
- Antimony chloride- \( \text{SbCl}_3 \)
- Anhydrous Sodium sulphite- \( \text{Na}_2\text{SO}_3 \)
- Selenium metal powder- \( \text{Se} \)
- Tellurium metal powder- \( \text{Te} \)
- Triethanolamine (TEA) - \( [\text{N(CH}_2\text{-CH}_2\text{-OH)}_3] \)

Preparation of precursor solutions

Bismuth tellurium selenide thin films have been prepared by an arrested precipitation technique by allowing the Bi-TEA complex to react with Te$^2$, Se$^2$ ions, which are released slowly by the dissociation of Na$_2$TeSO$_3$ and Na$_2$SeSO$_3$ in alkaline medium at pH 10.5. For the experiment all solutions were prepared in double distilled water.
**Bi-TEA complex**

0.05M Bismuth nitrate \([(\text{Bi(NO}_3)_3\cdot5\text{H}_2\text{O})]\) was prepared by triturating 2.425 gm Bismuth nitrate in 20ml triethanolamine (TEA) for six hours and diluted to 100ml with distilled water.

**Sb-TEA complex**

0.05M Antimony Chloride \([\text{SbCl}_3]\) solution was prepared by triturating 1.14 gm Antimony chloride in 20ml triethanolamine for six hours and diluted to 100 ml with distilled water.

**Sodium tellurium sulphite \((\text{Na}_2\text{TeSO}_3)\) solution**

0.05M Sodium tellurosulphite solution prepared by refluxing 30gm \(\text{Na}_2\text{SO}_3\) and 7 gm elemental tellurium metal powder in 250 ml distilled water at 100°C for 12 hours in a 250ml round bottom flask. After refluxing the solution was filtered and diluted to obtain 0.05M \(\text{Na}_2\text{TeSO}_3\).

**Sodium seleno sulphite \((\text{Na}_2\text{SeSO}_3)\) solution**

0.05 M Sodium seleno sulphite solution prepared by refluxing 30gm \(\text{Na}_2\text{SO}_3\) and 6 gm elemental selenium metal powder in 250 ml distilled water at 100°C for 6-7 hours in a 250 ml round bottom flask. After refluxing the solution was filtered and diluted to obtain 0.05M \(\text{Na}_2\text{SeSO}_3\).

### 4.3.2 Deposition of \(\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3\) thin films

Deposition bath was prepared by addition of 20 ml 0.05M bismuth triethanol ammine complex, 0.05 M \(\text{Na}_2\text{TeSO}_3\) \((1-x)\) and 0.05 M \(\text{Na}_2\text{SeSO}_3\) \((x)\) rest is water to make 100ml by adding distilled water in 150ml beaker. Where concentration of mixed phases are varied in the ratio \(x=0\) to\(1\). Thoroughly cleaned glass substrate was mounted on a substrate holder. The parameters such as pH of the bath was made 10.5 ± 0.2 by addition of 1:1 ammonia solution, time (2 hours), temperature of deposition bath (55 °C) and speed of substrate rotation (45±5 rpm) were optimized. After deposition, samples were taken out, washed with distilled water and kept in dark desiccators. Remaining all mixed bismuth tellurium selenide \(\text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3\) thin films were prepared by
varying concentrations of selenium and tellurium. Amount of Bi-TEA complex and its concentration were kept constant for all compositions. The concentrations of Te$^{2-}$, Se$^{2-}$ were varied in a volume stoichiometric ratio so as to obtain various compositions of Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin film. Table 4.1 shows the variations of Te$^{2-}$, Se$^{2-}$ in Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ in the film composition the samples were designated as F$_1$ to F$_7$ respectively.

Table 4.1 Composition of the sample for deposition of Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_1$</td>
<td>Bi$_2$Te$_3$</td>
</tr>
<tr>
<td>F$_2$</td>
<td>Bi$<em>2$(Te$</em>{0.8}$Se$_{0.2}$)$_3$</td>
</tr>
<tr>
<td>F$_3$</td>
<td>Bi$<em>2$(Te$</em>{0.6}$Se$_{0.4}$)$_3$</td>
</tr>
<tr>
<td>F$_4$</td>
<td>Bi$<em>2$(Te$</em>{0.5}$Se$_{0.5}$)$_3$</td>
</tr>
<tr>
<td>F$_5$</td>
<td>Bi$<em>2$(Te$</em>{0.4}$Se$_{0.6}$)$_3$</td>
</tr>
<tr>
<td>F$_6$</td>
<td>Bi$<em>2$(Te$</em>{0.2}$Se$_{0.8}$)$_3$</td>
</tr>
<tr>
<td>F$_7$</td>
<td>Bi$_2$Se$_3$</td>
</tr>
</tbody>
</table>

4.3.3 Deposition of Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$

Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films were prepared by keeping constant amount of the 15 ml sodium tellurium sulphite, 15 ml sodium seleno sulphite (Na$_2$SeSO$_3$) for the sources of Te$^{2-}$, Se$^{2-}$ respectively. Concentrations of Bi-TEA complex and Sb-TEA complex were varied in a volume stoichiometric ratio so as to obtain various compositions of Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films. Deposition of mixed Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films was carried out by keeping all the parameters similar to those finalised for the Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films. Table 4.2 shows film composition, the variations of Bi$^{3+}$, Sb$^{3+}$, Te$^{2-}$ and Se$^{2-}$ in Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ and their nomenclature. Where as Table 4.3 shows bath composition and preparative conditions for the Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films.
Table 4.2 Composition of the sample for deposition of Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_1$</td>
<td>Bi$<em>{1.98}$Sb$</em>{0.02}$(Te$<em>{0.5}$Se$</em>{0.5}$)$_3$</td>
</tr>
<tr>
<td>D$_2$</td>
<td>Bi$<em>{1.96}$Sb$</em>{0.04}$(Te$<em>{0.5}$Se$</em>{0.5}$)$_3$</td>
</tr>
<tr>
<td>D$_3$</td>
<td>Bi$<em>{1.94}$Sb$</em>{0.06}$(Te$<em>{0.5}$Se$</em>{0.5}$)$_3$</td>
</tr>
<tr>
<td>D$_4$</td>
<td>Bi$<em>{1.92}$Sb$</em>{0.08}$(Te$<em>{0.5}$Se$</em>{0.5}$)$_3$</td>
</tr>
<tr>
<td>D$_5$</td>
<td>Bi$<em>{1.90}$Sb$</em>{0.1}$(Te$<em>{0.5}$Se$</em>{0.5}$)$_3$</td>
</tr>
</tbody>
</table>

4.4 Effect of preparative parameters on deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films

Effect of preparative parameters on deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films are discussed as below

4.4.1 Geometry of the substrate holder

The holder was fabricated by using Bakelite material of appropriate thickness. It is a circular disc slotted to fix the substrate in such a fashion that each of the substrate was exactly perpendicular to each other. The continuous proper bulk churning of the solution in the reaction container was made possible which help in depositing uniform and better orientation of the crystallites. In order to rotate the substrate in a reaction container the substrate holder is attached to rotating shaft of constant speed, A. C. gear Remi make electric motor. A specially designed substrate holder as shown in Figure 4.3 A and 4.3 B was used for holding the substrate in vertical position.

4.4.2 Speed of substrate rotation

Speed of the substrate rotation in present research work was kept fixed at an optimum value 45 ± 5. Because during the deposition of the metal chalcogenide thin films speed of the substrate rotation plays an important role. At lower speed (<35 rpm) thick less adherent and porous films were obtained, while at higher speed (>60 rpm) reflecting and very thin adherent films were deposited over glass substrate. Therefore speed of the substrate
rotation was kept at an optimum value 45±5 rpm so as to form highly reflecting, stiochemtric, uniform and adherent thin films.

4. 4. 3 Bath compositions

The quality and growth rate of the deposited films was greatly influenced by the concentration of the reacting species. Therefore we have studied the effect of the concentration of the reacting species for various concentrations. The film deposited by using low concentration is thin and non uniform. This observation can be related to the insufficient supply of ionic species at such concentration levels. On the other hand when concentration of the species was increased, the quality and uniformity of the films goes on increasing and the films were thick. This is true up to a certain level of concentration and then saturation in the growth process was observed. Ternary Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ uniform films were obtained for the 0.05M solution after deposition period of 2 hours and at 55°C. The deposition was carried out for of the constant Bi-TEA volume and different volume ratios of sodium tellurosulphite and sodium selenosulphite solution. It was observed that the films obtained are smooth and uniform, when corresponding volume ratio was 2 : 1-x : x for Bi$_2$(Te$_{1-x}$Se$_x$)$_3$.

The Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films were obtained for the 0.05M solution after deposition period of 2 hours and at 55°C. The deposition was carried out for of the different volumes of Bi-TEA, Sb-TEA and constant volume ratios of sodium tellurosulphite and sodium selenosulphite solution. It was observed that the films obtained are smooth and uniform, when corresponding volume ratio was 2-x: x: 0.5:0.5 for Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$.

4. 4. 4 pH of reacting mixture

Increase in the pH value causes increase in the relative molecular surface area and solubility. In order to improve the above conditions for the film formation, the $p^H$ value of the bath solution was varied from 8.0 to 11 for ternary Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb(III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ series. At pH 10.5 adherent and uniform thin films are obtained. In chemical growth process used for deposition of thin films largely depends on the pH value of reacting
solution. It was observed that at lower pH values precipitation was fast and hence no film was deposited. At the higher pH values, precipitation became slower and films were deposited in the forms of patches.

4.4.5 Deposition time

Growth of the thin film is time dependent. The temperature of the bath directly affects the growth of thin films. The Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ film growth involves the reaction of bismuth ions with telluride ions and selenide ions in basic medium. At a temperature rate of 55 °C, the film growth starts after an initial nucleation period of about 30 minutes. A blackish-gray precipitate gradually fills the bath. The growth rate slows down after deposition period of 2 hours. So deposition after 2 hours results in less material formation on the substrate. This time was finalized by studying the growth rate for various deposition durations. After addition of reactants reaction can be starts. Which can be observed by change in colour and ultimately it ends in deposition of film. Deposition time is optimized by taking a substrate out of bath at regular intervals of time period. For ternary Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films colour of the films changes from gray to black as concentration of tellurium decreases.

The Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ series film growth involves the reaction of bismuth ions, antimony ions with telluride and selenide ions in the basic medium. At temperature rate of 55 °C, the film growth starts after an initial nucleation period of 30 minutes. A grayish black precipitate appears after about 2 hours. It was found that layer thickness increased with the deposition time and later on it saturates.

4.4.6 Constant deposition temperature bath

The effect of bath temperature on the growth of chemically deposited thin films can be very extreme with respect to the terminal thickness, morphology, optical and electronic properties. The rate of deposition increases with the bath temperature. This is expected because of the increase in concentrations of Bi$^{3+}$/Sb$^{3+}$, Te$^{2-}$ and Se$^{2-}$ ions in the bath due to enhanced dissociation of the metal ion complex, sodium tellurium sulphite and sodium seleno sulphite solution at higher temperatures. Such behaviour is common in the chemical bath deposition of metal chalcogenide thin films [16]. Thus
duration of deposition can be reduced by increase in temperature. With an increase of bath temperature from 45 to 65 °C, the rate of deposition of Bi$_2$Se$_3$ films decreases due to an increase in the kinetic energy of the reacting ions. The optimized deposition temperature is 55 °C for ternary Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films.

4. 4. 7 Complexing agents

The formation of complex ion is essential to control the rate of reaction and to avoid the immediate precipitation of the compound in the solution. A complexing agent used to bind metallic ions to avoid the homogenous precipitation of the corresponding compound. Bi$^{3+}$ and Sb$^{3+}$ ions immediately reacts with Te$^{2-}$ and Se$^{2-}$ ions to form insoluble Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ precipitate.

![a) Bi$^{3+}$-TEA Complex](image1.png)  ![b) Sb$^{3+}$-TEA Complex](image2.png)

**Figure 4.4** Probable structure of Bi-TEA and Sb-TEA complex.
Table 4.3 Bath composition and preparative conditions for the Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films

<table>
<thead>
<tr>
<th>Film composition</th>
<th>Bath composition</th>
<th>Preparative conditions</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>2$(Te$</em>{1-x}$Se$_x$)$_3$ (F$_1$ to F$_7$)</td>
<td>20 ml 0.05 M Bi-TEA + 0.05 M Na$_2$TeSO$_3$ (1-x) and 0.05 M Na$_2$SeSO$_3$ (x) rest is water to make 100 ml total volume. Where concentration of mixed phases are varied in the ratio x=0 to 1</td>
<td>pH = 10.5 ± 0.3 Temperature = 55 ± 0.5 °C Deposition time = 2 hrs Substrate rotation = 45 ± 5 rpm</td>
<td>Between 0.21µm to 0.71µm</td>
</tr>
<tr>
<td>Sb (III) doped Bi$<em>2$(Te$</em>{1-x}$Se$_x$)$_3$ (D$_1$ to D$_5$)</td>
<td>(20 –x) ml 0.05 M Bi-TEA + x ml 0.05 M Sb-TEA + 15 ml 0.05 M Na$_2$TeSO$_3$ +15ml 0.05M Na$_2$SeSO$_3$ and rest is water to make 100 ml total volume. x is varied from 0.0 to 0.1 ml</td>
<td>pH = 10.5 ± 0.3 Temperature = 55 ± 0.5 °C Deposition time = 2 hrs Substrate rotation = 45 ± 5 rpm</td>
<td>Between 0.19µm to 0.80µm</td>
</tr>
</tbody>
</table>

At such rapid rate of reaction deposition of desired metal chalcogenide on substrate material could not be possible. Hence in order to slow down the rate of reaction Bi$^{3+}$ and Sb$^{3+}$ ions are arrested by using suitable complexing agent. The metal complex hydrolyses slowly at basic pH to generate the positive ions (Bi$^{3+}$ and Sb$^{3+}$) in the solutions. Triethanolamine was used as complexing agent for bismuth (III) and antimony (III) ions. Figure 4.4 shows the probable structure of a) Bi-TEA complex and b) Sb –TEA complex. Table 4.3 shows bath composition and preparative conditions for the Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films.

4.5 Growth mechanism of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin film formation

During the deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films growth mechanism depends on the material being deposited and other parameters such as reaction time, temperature, complexing agent, pH etc. It includes three phases namely nucleation phase, growth phase and a terminal phase [17].
In arrested precipitation technique, a complexing agent is used to bind the metallic ions to avoid the homogeneous precipitation of the corresponding compound. The formation of complex ion is essential to control the rate of reaction and to avoid the immediate precipitation of compound in the solution. During the reaction the metal complex hydrolyses slowly and generates the positive ions in solution. These ions mixed with a solution producing negative ions. If solution is saturated, then the ionic product exceeds the solubility product and ions deposits on the substrate to form the nuclei. The presence of the surface of a substrate introduces a degree of homogeneity that facilitates nucleation in film growth processes. Therefore, the surface of the substrate can be considered a catalyst which activates the nucleation. Once nucleation starts on a substrate, it becomes easier for the film formation. Since deposition usually occurs more easily on the nucleated surface than on the clean surface. On the substrate either homogeneous or heterogeneous deposition can occur. The homogeneous process is the faster one, resulting in the adsorption of powdery particles on the substrate due to the bulk precipitation. In the heterogeneous process, the preferential adsorption of Bi$^{3+}$, Te$^{2-}$ and Se$^{2-}$ ions will take place, leading to the uniform nucleation and growth of the thin film. So, the formation of metal complex is essential to minimise the homogeneous process. Addition of NH$_4$OH increases the OH$^{-}$ ion concentration in the solution and that favours the hydrolysis of the chalcogen precursor.

APT is suitable for the deposition of Bi$_2$ (Te$_{1-x}$ Se$_x$)$_3$ mixed type thin films. According to Ostwald ripening law if metal ions in solution are arrested using polydentate complexing agent like TEA, the rate of reaction between metal ions and chalcogenide ions can be well controlled to get desired quality of metal chalcogenide thin films. In the present investigation, we have slightly modified the chemical deposition method using polydentate chelating agent, triethanolamine [N(CH$_2$-CH$_2$-OH)$_3$] as a complexing agent to arrest Bi$^{3+}$ ions. The stability constant indicates strong affinity of the organic complexing agent TEA towards the Bi$^{3+}$ ions and its tendency to keep the Bi$^{3+}$ ion arrested in a solution even in alkaline pH range, where the metal hydroxide formation is possible. Concentration of precursors also shows strong influence on the growth of Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films. In the present investigation ionic species of
Bi$^{3+}$, Te$^{2-}$ and Se$^{2-}$ are produced as per the following reaction equilibria [18, 19].

During the deposition process Bi$^{3+}$, Te$^{2-}$ and Se$^{2-}$ ions are slowly released in the solution in an aqueous alkaline deposition bath. The formation of Bi$_{2}$(Te$_{1-x}$Se$_{x}$)$_{3}$ thin films occur when ionic product of Bi$^{3+}$, Te$^{2-}$, and Se$^{2-}$ exceeds the solubility product of Bi$_{2}$(Te$_{1-x}$Se$_{x}$)$_{3}$. Overall growth mechanism of the mixed composites of Bismuth tellurium selenide are summarized as follows.

\[
(\text{NH}_{4})_{3}[\text{Bi}_{2}\text{N(CH}_2\text{CH}_2\text{-O)}_3] + 6\text{H}_2\text{O} \rightarrow \text{Bi}^{3+} + 3\text{NH}_4\text{OH} + 3\text{OH}^{-} + 2[\text{N(CH}_2\text{CH}_2\text{-OH)}_3] \quad (4.1)
\]

\[
\text{Na}_2\text{TeSO}_3 + \text{OH}^{-} \rightarrow \text{Na}_2\text{SO}_4 + \text{HTe}^{-} \quad (4.2)
\]

\[
\text{HTe}^{-} + \text{OH}^{-} \rightarrow \text{H}_2\text{O} + \text{Te}^{2-} \quad (4.3)
\]

\[
\text{Na}_2\text{SeSO}_3 + \text{OH}^{-} \rightarrow \text{Na}_2\text{SO}_4 + \text{HSe}^{-} \quad (4.4)
\]

\[
\text{HSe}^{-} + \text{OH}^{-} \rightarrow \text{H}_2\text{O} + \text{Se}^{2-} \quad (4.5)
\]

The reactions given in equation (4.1) to (4.5) shows that the Bi$^{3+}$, Te$^{2-}$ and Se$^{2-}$ are condenses ion by ion basis on the glass substrate at pH 10.5 and 55°C temperature as follows:

\[
\text{Bi}^{3+} + n\text{Na}_2\text{TeSO}_3, n\text{Na}_2\text{SeSO}_3 \rightarrow \text{Bi}_2(\text{Te}_{1-x}\text{Se}_x)_3, n\text{Na}_2\text{SO}_4 + n(\text{TEA}) \quad (4.6)
\]

TEA is stable throughout the deposition period and temperature. Finally, the deposited Bi$_{2}$(Te$_{1-x}$Se$_{x}$)$_{3}$ films prepared by arrested precipitation technique are found to be uniform and well adherent to the substrate. Chemical reaction is followed by annealing in order to form stable single phase solid solutions. After annealing, specimens are cut into pieces of different size for measurement purposes and to enhance the mechanical and thermoelectric properties.

4. 6 Growth mechanism of Sb (III) doped Bi$_{2}$ (Te$_{1-x}$Se$_{x}$)$_{3}$ thin film formation

Arrested precipitation technique is also suitable for the deposition of Sb (III) doped Bi$_{2}$(Te$_{1-x}$Se$_{x}$)$_{3}$ mixed type thin films. In the present investigation, we have slightly modified the chemical deposition method using polydentate chelating agent such as triethanolamine [N (CH$_2$-CH$_2$-OH)$_3$] as a complexing agent to arrest Bi$^{3+}$ and Sb$^{3+}$ ions. Organic complexing agent TEA have strong
affinity towards the Bi$^{3+}$ and Sb$^{3+}$ ions and it's tendency to keep the Bi$^{3+}$ and Sb$^{3+}$ ion arrested in a solution even in alkaline pH range where the metal hydroxide formation is possible. Here ionic species of Bi$^{3+}$, Sb$^{3+}$, Te$^{2-}$ and Se$^{2-}$ are produced as per the following reaction equilibria.

Bi$^{3+}$, Sb$^{3+}$, Te$^{2-}$ and Se$^{2-}$ ions are slowly released in the solution in an aqueous alkaline medium to deposite Sb(III) doped Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ thin films. The formation of Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films occurs when ionic product of Bi$^{3+}$, Sb$^{3+}$, Te$^{2-}$ and Se$^{2-}$ exceeds the solubility product of Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$. Overall growth mechanism of the mixed composites of bismuth antimony tellurium selenide is summarized as follows.

\[(\text{NH}_4)_3[\text{Bi}_2\text{N(\text{CH}_2\text{-CH}_2\text{-O})_3}]+6\text{H}_2\text{O} \rightarrow \text{Bi}^{3+}+3\text{NH}_4\text{OH}+3\text{OH}^-+2[\text{N(\text{CH}_2\text{-CH}_2\text{-OH})_3}] \quad (4.7)\]

\[(\text{NH}_4)_3[\text{Sb}_2\text{N(\text{CH}_2\text{-CH}_2\text{-O})_3}]+6\text{H}_2\text{O} \rightarrow \text{Sb}^{3+}+3\text{NH}_4\text{OH}+3\text{OH}^-+2[\text{N(\text{CH}_2\text{-CH}_2\text{-OH})_3}] \quad (4.8)\]

\[\text{Na}_2\text{TeSO}_3 + \text{OH}^- \rightarrow \text{Na}_2\text{SO}_4 + \text{HTe}^- \quad (4.9)\]

\[\text{HTe}^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Te}^{2-} \quad (4.10)\]

\[\text{Na}_2\text{SeSO}_3 + \text{OH}^- \rightarrow \text{Na}_2\text{SO}_4 + \text{HSe}^- \quad (4.11)\]

\[\text{HSe}^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Se}^{2-} \quad (4.12)\]

The reactions given in equation (4.7) to (4.12) shows that the Bi$^{3+}$, Sb$^{3+}$, Te$^{2-}$ and Se$^{2-}$ are condenses ion by ion basis on the glass substrate at pH 10.5 and 55°C temperature as follows:

\[\text{Bi}^{3+}\text{Sb}^{3+}n\text{Na}_2\text{TeSO}_3, n\text{Na}_2\text{SeSO}_3 \rightarrow \text{Bi}_2\text{Sb}_x(\text{Te}_{1-x}\text{Se}_x)_3, n\text{Na}_2\text{SO}_4 + n(\text{TEA}) \quad (4.13)\]

Finally, the deposited Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ films prepared by arrested precipitation technique are found to be uniform and well adherent to the substrate.

4.7 Conclusion

APT is simple, low cost and suitable method. In conclusion, this communication demonstrates that ternary Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb (III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ thin films have been successfully deposited using APT at low temperature. The arrested precipitation technique (APT) is found to be most convenient method for deposition of Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ and Sb(III) doped Bi$_2$ (Te$_{1-x}$Se$_x$)$_3$ mixed metal chalcogenide thin films.
References
