Section A

As Deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films

4.A.1 Introduction

The efficiency of thermoelectric devices depends on several properties of materials which can be quantified by dimensionless figure of merit (ZT). Thermoelectric materials and cells have attracted considerable interest due to the requirement of environment protection and other applications such as power generation, refrigeration etc. Bismuth telluride and its derivatives with selenium compounds have considerable TE properties which are used by the military for night vision equipment, electronic equipment cooling, portable refrigerators and internal guidance system [1]. Bi$_2$Te$_3$, Bi$_2$Se$_3$, MoTe$_2$, MoSe$_2$ and their solid solution crystals are narrow band gap semiconductors with asymmetric band structure, having rhombohedral unit cell. Optical band gap energies for these materials varies from 0.15 to 1.4 eV (Bi$_2$Te$_3$), 0.14 to 2.35 eV (Bi$_2$Se$_3$), 0.6 to 1.0 eV (MoTe$_2$) and 1.12 to 1.52eV (MoSe$_2$) respectively[2-5].

Recently there has been a great deal of interest in the study of ternary and quaternary chalcopyrite compounds. Most recently S. M. Patil et. al [6] reported the synthesis and thermoelectric properties of Bi$_2$(Te$_{0.5}$Se$_{0.5}$)$_3$ thin films with 0.1 ZT. Influence of tellurium concentration on properties of MoSe$_{2-x}$Te$_x$ thin films has been reported by Bernede et. al [7]. Electrical properties of crystalline Pb$_x$Sn$_{1-x}$Te$_{0.5}$Se$_{0.5}$ [8], CuIn(Se$_2$)$_2$ [9] films has been reported which shows small efficiency in thermoelectric devices. Amongst quaternary chalcogenides, Bi$_{2-x}$Sb$_x$Te$_3$Se$_y$ [10] is best known thermoelectric material that has long served for cooling applications from ambient temperature (ZT≈1).

To the best of our knowledge, there is no single report available for quaternary Mo-Bi-Se-Te system. In the present chapter we discuss the synthesis of quaternary MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films by Arrested Precipitation Technique (APT). The same technique had been used by our group for deposition of various Chalcogenide thin films [2-4]. The purpose of present work is to establish and optimize the growth conditions to produce good quality
fibrous reticulate porous framework of nanocrystalline MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. Therefore we have tried to optimize variable concentration of Se and Te to maximize thermoelectric ZT properties of resulting composite materials.

4. A. 2 Experimental Details for Deposition of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films

Experimental set up used for deposition of quaternary MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is same as discussed in Chapter III (Section 3.2). Thin films of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ were prepared by APT employing Analytical Reagent (AR) grade chemicals manufactured by Merck and Hi-media, which was discussed in Chapter III (section 3.3.2). The sodium selenosulphide (Na$_2$SeSO$_3$) solution was prepared by refluxing 6 g of selenium metal powder (Se) and 30 g Sodium sulphite (Na$_2$SO$_3$) in 250 ml distilled water at 100°C for 8 hours in a 500 ml round bottom flask. After 8 hours refluxing, the clear solution was obtained. Preparation of rest of solutions is same as that discussed in chapter 3 (Section 3.3.2).

Deposition of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films have been prepared by using APT, it allows the Bismuth-Triethanolamine (Bi-TEA) and Molybdenum-Triethanolamine (Mo-TEA) complex to react with Se$^{2-}$, Te$^{2-}$ ions which are released slowly by the dissociation of Na$_2$SeSO$_3$ and Na$_2$TeSO$_3$ in alkaline medium at pH 9.5 and temperature 55°C. The nucleation and growth of quaternary thin films depends on the material being deposited and the other parameters such as concentration of precursor solutions, reaction time, temperature, complexing agent and pH. These preparative parameters were optimized during initial stages of experiment. The concentration of Bi-TEA and Mo-TEA complex were kept constant for all compositions. The concentrations of Na$_2$SeSO$_3$ and Na$_2$TeSO$_3$ were varied in a volume stoichiometric ratio x (0.0, 0.2, 0.5, 0.6, 0.7, 0.8 and 1 mL) so as to obtain various compositions of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films and they are abbreviated as a, b, c, d, e, f and g respectively as shown in table 4.1. At the end, the deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ films are found to be uniform and well adherent to the substrate.
Table 4.1 Bath composition and optimized preparative parameters for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Composition</th>
<th>Bath composition</th>
<th>Optimized preparative parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>MoBi$_2$Se$_5$</td>
<td>4 ml Mo-TEA + 16 ml Bi-TEA + 1-x ml 0.25 M Na$_2$SeSO$_3$ + x ml 0.25 M Na$_2$TeSO$_3$, rest is water to make 100 ml total volume. Where concentration of mixed phases are varied in the ratio x=0.0 to 1.0</td>
<td>pH = 9.5 ± 0.2</td>
</tr>
<tr>
<td>b</td>
<td>MoBi$<em>2$(Se$</em>{0.8}$Te$_{0.2}$)$_5$</td>
<td></td>
<td>Temperature = 55± 0.5°C</td>
</tr>
<tr>
<td>c</td>
<td>MoBi$<em>2$(Se$</em>{0.5}$Te$_{0.5}$)$_5$</td>
<td></td>
<td>Deposition time = 3 hours</td>
</tr>
<tr>
<td>d</td>
<td>MoBi$<em>2$(Se$</em>{0.4}$Te$_{0.6}$)$_5$</td>
<td></td>
<td>Substrate rotation = 45 ± 5 rpm</td>
</tr>
<tr>
<td>e</td>
<td>MoBi$<em>2$(Se$</em>{0.3}$Te$_{0.7}$)$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>MoBi$<em>2$(Se$</em>{0.2}$Te$_{0.8}$)$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>MoBi$_2$Te$_5$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.A.3 Mechanism of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Film Formation

In APT the metal ions in solution are arrested by using polydentate complexing agent which controls the rate of reaction between metal ions and chalcogen ions. The release of metal ions takes place at the specific pH and temperature. As mentioned in table 4.1, the deposition of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were carried out. The pH 9.5 and temperature 55°C were maintained for deposition of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. It is well known that at alkaline pH the concentration of OH$^-$ ions increases with slow dissociation of Bi-TEA and Mo-TEA complexes which results in the release of Mo$^{4+}$ and Bi$^{3+}$ ions [11]. Also in the alkaline pH controlled release of Se$^{2-}$ and Te$^{2-}$ ions from Na$_2$SeSO$_3$ and Na$_2$TeSO$_3$ aqueous solution. Therefore at optimized alkaline pH 9.5 growths of thin films took place. Also the temperature of chemical bath plays an important role during the growth of the thin film by using APT. At room temperature the rate of reaction is very slow for the release of metal ions from its complex. Hence whole chemical bath was maintained at 55°C which causes an increase in rate of release of metal ions making them available for the reaction to takes place. According to Ostwald ripening law [12] if small
nucleus or embryo is close to a larger crystal, the ions formed by particle dissolution of the smaller and less stable crystal can be incorporated into the larger crystal, and the film formation takes place by the growth of metal chalcogenides according to ion-by-ion condensation. When the time reaches all the ions in the solution vanishes called terminal growth phase which results in formation of fibrous reticulate framework of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. Schematic representation of formation of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ fibrous reticulate porous framework is shown in figure 4.1.

Schematic representation of formation of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$

Overall growth mechanism for the mixed metal chalcogenide thin film of Molybdenum bismuth selenotelluride is summarized as follows:

\[
(NH_4)_2[Mo2N(CH_2-CH_2-O)_3] + 2(NH_3)[Bi2N(CH_2-CH_2-O)_3] + nNa_2SeSO_3 + nNa_2TeSO_3 + nH_2O
\]

\[
pH 9.5
\]

\[
MoBi$_2$(Se$_{1-x}$Te$_x$)$_5 + 6[N(CH_2-CH_2-OH)_3] + 8(NH_3)OH + nNa_2SO_4
\]

At pH 9.5 and temperature 55°C the ionic product of Bi$^{3+}$, Mo$^{4+}$, Se$^{2-}$ and Te$^{2-}$ ions exceeds the solubility product of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ in the reaction bath, which results in ion-by-ion condensation on glass substrate. Here TEA is stable throughout the deposition period and temperature.
4.A.4 Characterization of As Deposited Quaternary MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films

4.A.4.1 Thickness Measurement

Thickness of as deposited thin films were measured by using the surface profilometer (Model: XP-1 Ambios Technolony) having 1 Å resolution as discussed in Chapter II (Section 2.3.1.1). It is observed that, terminal thickness of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films deposited by using APT ranges from 237 to 314 nm as listed in table 4.2.

4.A.4.2 UV-Visible Absorption Spectra

The optical absorption study was carried out using UV-Visible spectrophotometer (Model: Shimadzu, UV Probe-1800 Japan). Measurement of optical absorbance for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were carried out in the wavelength range 300-800 nm. Plot of $(\alpha h \nu)^2$ Vs Photon Energy ($h \nu$) for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films shown in figure 4.2.

Figure 4.2 Plot of $(\alpha h \nu)^2$ Vs Photon Energy ($h \nu$) for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

4.A.4.3 X-ray Diffraction (XRD)

X-ray diffraction studies were carried out using X-ray diffractometer [Bruker AXS Model D8 Advance X –ray Diffractometer] with Cu Kα target having wavelength 1.542Å between the 2θ angle ranges from 20 to 80°. The
X-ray patterns for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films deposited by APT is shown in figure 4.3.

Figure 4.3 XRD patterns for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

4.A.4.4 Scanning Electron Microscopy (SEM)

Surface morphology of films was studied using scanning electron microscopy [SEM: JEOL JSM-6360A Analytical Scanning Electron Microscope]. The SEM images for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films having varying concentration are given in figure 4.4.
Figure 4.4 SEM images for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films
4.A.4.5 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) was performed on JSM-5200 microscope. Atomic Force Microscopy (AFM) has been proven to be a well known method to analyze the surface morphology of thin films. Figure 4.5 shows (f1) 2D and (f2) 3D AFM images of as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films respectively.

![Figure 4.5 (f1) 2D and (f2) 3D AFM images of as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films](image)

4.A.4.6 Transmission Electron Microscopy (TEM)

Transmission Electron Microscope (TEM) utilizes energetic electrons to provide morphological, compositional and crystallographic information on sample. One of the first applications of TEM is to study the particle size, shape and size distribution of particles. A second application of TEM is the identification of crystal structure of crystalline particles by electron diffraction. The diffraction pattern is in form of concentric rings or series of rings. Each ring or series of spots corresponds to a particular set of crystal planes. Figure 4.6 shows (f1) 100 nm magnification TEM images (f2) SAED pattern for as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films.

![Figure 4.6](image)
Figure 4.6 (f1) 100 nm magnification TEM images (f2) SAED pattern for the as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin film

4.A.4.7 Energy Dispersive X-ray Spectroscopy (EDS)

The compositional analyses were carried out using Energy Dispersive X-ray Spectroscopy (EDS) [EDS: JEOL JSM-6360A Analytical Scanning Electron Microscope]. The EDS pattern for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films deposited by APT are shown in figure 4.7.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Expected At. %</th>
<th>Actual At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>12.50</td>
<td>11.08</td>
</tr>
<tr>
<td>Bi</td>
<td>25.00</td>
<td>30.54</td>
</tr>
<tr>
<td>Se</td>
<td>62.50</td>
<td>57.66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
<th>Expected At. %</th>
<th>Actual At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>12.50</td>
<td>11.08</td>
</tr>
<tr>
<td>Bi</td>
<td>25.00</td>
<td>28.35</td>
</tr>
<tr>
<td>Se</td>
<td>31.25</td>
<td>34.87</td>
</tr>
<tr>
<td>Te</td>
<td>31.25</td>
<td>25.70</td>
</tr>
</tbody>
</table>
Synthesis and Characterization of MoBi$_2$(Te$_{1-x}$Se$_x$)$_5$ Thin Films

4.A.4.8 X-ray Photoelectron Spectroscopy (XPS)

Binding energy, elemental composition and surface nature of MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films is confirmed by using XPS. The XPS data were collected in the constant analyzer energy mode at 20eV. Mg Ka (hν = 1253.6 eV) radiation was employed as the excitation source with an anode voltage of 15 kV and an emission current of 20 mA. The survey and core level spectra of the Mo 3d, Bi 4f, Se 3d and Te 3d are obtained using C 1s as reference at 284.6 eV. The XPS plots for as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ sample are shown in figure 4.8.
Figure 4.8 XPS Spectrum of as deposited MoBi$_2$(Te$_{1-x}$Se$_x$)$_5$
(a) Survey spectrum (b) Core level spectrum of Mo 3d (c) Core level spectrum of Bi 4f (d) Core level spectrum of Se 3d (e) Core level spectrum of Te 3d

4.4.9 Electrical Conductivity (EC)

The measurements of Electrical Conductivity (EC) of as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were carried out in temperature range 300-500 K on 1x1 cm$^2$ area of samples, using standard DC two point probe method. Plots of $\ln \sigma$ vs 1000/T for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.9.
Figure 4.9 Plots of ln $\sigma$ vs $1000/T$ for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

4.A.4.10 Thermoelectric Power (TEP) Measurement

The type of conductivity of as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is determined from Thermoelectric Power (TEP) measurement. Thermoelectric properties of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were measured in the temperature range 300 to 500 K. Figure 4.10 shows variation of Seebeck coefficient (S) vs Temperature for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.

Figure 4.10 Plots of Seebeck coefficient (S) vs Temperature for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films
Carrier concentration (n)

The carrier concentration of charge carriers were calculated and plot of log n vs 1000/T is shown in figure 4.11 for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.

![Figure 4.11 Plots of log n vs 1000/T for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films](image)

Mobility (µ)

The mobility of charge carriers were calculated and plot of log µ vs 1000/T is shown in figure 4.12 for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.

![Figure 4.12 Plot of log µ vs 1000/T for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films](image)
Plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs Te content is shown in figure 4.13 for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.

Figure 4.13 Plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs Te content for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

Table 4.2 Observed variation of thickness, crystallite size, band gap and activation energy for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample id</th>
<th>Film thickness(nm)</th>
<th>Crystallite Size nm</th>
<th>Band gap (eV)</th>
<th>Activation Energy (ΔE) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoBi$_2$Se$_5$</td>
<td>a</td>
<td>237</td>
<td>20.8</td>
<td>1.78</td>
<td>0.0321</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.8}$Te$_{0.2}$)$_5$</td>
<td>b</td>
<td>242</td>
<td>24.9</td>
<td>1.63</td>
<td>0.0307</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.5}$Te$_{0.5}$)$_5$</td>
<td>c</td>
<td>250</td>
<td>26.7</td>
<td>1.57</td>
<td>0.0284</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.4}$Te$_{0.6}$)$_5$</td>
<td>d</td>
<td>264</td>
<td>28.4</td>
<td>1.54</td>
<td>0.0256</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.3}$Te$_{0.7}$)$_5$</td>
<td>e</td>
<td>280</td>
<td>30.2</td>
<td>1.5</td>
<td>0.0221</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.2}$Te$_{0.8}$)$_5$</td>
<td>f</td>
<td>305</td>
<td>35.7</td>
<td>1.46</td>
<td>0.0208</td>
</tr>
<tr>
<td>MoBi$_2$Te$_5$</td>
<td>g</td>
<td>314</td>
<td>38.4</td>
<td>1.44</td>
<td>0.0175</td>
</tr>
</tbody>
</table>

4.A.4.11 Results and Discussion

The optical absorption coefficient (α) of as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films with different compositions were calculated using the absorbance value measured for a particular wavelength (λ) and film thickness (t). In the higher region (α >10$^4$ cm$^{-1}$) the relation between the absorption coefficient (α) and the incident photon energy (hν) is discussed in Chapter II (section 2.1). The values of the (αhν)$^2$ Vs Photon Energy (hν) plots and corresponding band gaps
were obtained from extrapolating the straight line portion of the graph on hv axis at α=0.

Figure 4.2 shows plot of (αhv)^2 vs Photon Energy (hv) for as deposited MoBi₂(Se₁₋ₓTeₓ)₅ thin film. The nature of plot suggests direct allowed type of transition. Table 4.2 shows values of optical band gap of the as deposited MoBi₂(Se₁₋ₓTeₓ)₅ thin films. The optical band gap (Eg) is strongly dependent on the concentration of Te. It is found that the Eg decreases gradually from 1.78 to 1.44 eV with increase in Te content in as deposited MoBi₂(Se₁₋ₓTeₓ)₅ thin films. The effect of electronegativity contributes to the width of the band gap. The electronegativities of Mo, Bi, Se and Te are 2.16, 2.02, 2.55 and 2.1 respectively. According to these values it is noticed that Te is less electronegative than Se. Consequently the substitution of Se by Te raise the energy and hence broaden the valance band thereafter decreases the optical band gap.

Figure 4.3 shows XRD patterns of the as deposited MoBi₂(Se₁₋ₓTeₓ)₅ thin films. The broad, low intense peaks in all samples indicate nanocrystalline nature of thin films. The diffraction peaks for as deposited MoBi₂Se₅ thin films are found at 2θ values 39.5°, 58.7° and 76.7° degree corresponding to lattice planes (311), (025) and (2012) respectively. After addition of Te the diffraction peaks becomes sharp, appear at lower 2θ values are found at 23.20°, 27.60°, 29.36°, 30.54°, 32.84°, 38.20° and 43.63° degree corresponding to lattice planes (101), (211), (003), (300), (012) and (440) respectively. The diffraction peaks for as deposited MoBi₂Te₅ thin films are found at 29.7°, 38.20°, 45.00° and 53.10° degree corresponding to lattice planes (015), (104) (321) and (208) respectively. No other impurity peaks were observed, it shows purity of the sample. There are no standard JCPDS data available for different compositions of as deposited MoBi₂(Se₁₋ₓTeₓ)₅ thin films. The plane indices are obtained by comparing the intensities and positions of peaks with these Bi₂Te₃, Bi₂Se₃, MoTe₂ and MoSe₂ binary systems which are given by JCPDS card no. 08-0027, 72-2123, 23-1257 and 72-1420 respectively with rhombohedral crystal structure.
where ‘d’ is interplaner distance, ‘a’ is lattice parameter and θ is Bragg’s angle for prominent peak. For rhombohedral crystal structure, lattice parameters are a=b=c (intercepts) and α=β=γ≠90° (crystal structure). The value of lattice parameter was calculated from the (hkl) planes by using the equation 4.8 [10].

In figure 4.3 the prominent peak observed at 2θ = 29.36˚ having (hkl) plane (003). The calculated value of lattice parameter ‘a’ at prominent peak is 5.81Å, which is in good agreement with standard JCPDS data. The crystallite sizes were calculated by using Debye-Scherer equation discussed in Chapter II (section 2.6). The crystallite size increases from 20.8 to 38.4 nm after increasing Te content in as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. Increase in the crystallite size with Te addition is related with the decrease in band gap [11, 12].

The surface morphology of the as deposited thin films was determined by SEM as shown in figure 4.4. The SEM micrographs show uniform film surface without cracks. It is observed that fibrous reticulate porous framework does not get disturbed as Te content increases but increase in the film thickness is observed. It reveals that, as addition of tellurium increases the area of fibrous reticulate porous framework increases, therefore the structure becomes more compact and because of this granular morphology is observed for the g composition. This may occurs because, as tellurium is larger in size than selenium, the average size goes on increasing after addition of tellurium. The increase in tellurium content in as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films plays an important role in defining the surface properties like fiber distribution, porosity etc. Generally, semiconductor films with porous structure showed improved performance in thermo cooling applications [13].

Figure 4.5 shows (f1) 2D and (f2) 3D AFM images of as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films. The film surface was well covered with fibrous reticulate porous framework for MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films. In the 3D image,
an intense strip is shown that indicates the surface fibers along the z axis. The AFM images are in well agreement with the SEM images and reveal a low level of roughness i.e. 5.40 nm/1µm².

Figure 4.6 shows TEM images for as deposited MoBi₂(Se₀.₂Te₀.₈)₅ thin films. Figure 4.6 (f1) shows TEM image for 100 nm magnification, it reveals that the particles are agglomerates and fibrous reticulate porous framework in nature. Figure 4.6 (f2) shows the selected area electron diffraction (SAED) pattern for as deposited MoBi₂(Se₀.₂Te₀.₈)₅ thin films. The lattice planes (101), (211), (003), (300) and (012) are observed in SAED pattern. It indicates that as deposited MoBi₂(Se₀.₂Te₀.₈)₅ thin films in rhombohedral crystal structure, which is in accordance with the XRD results.

The quantitative analyses of Mo, Bi, Se and Te in the sample were performed by the use of EDS at different points. Figure 4.7 shows the spectral distribution of the constituent elements for typical MoBi₂(Se₁₋ₓTeₓ)₅ samples. The atomic percentages of Mo, Bi, Se and Te in as deposited thin films of MoBi₂(Se₁₋ₓTeₓ)₅ are listed in inset of figure 4.7 which clearly shows that, theoretical and practical atomic percentage of Mo, Bi, Se and Te in MoBi₂(Se₁₋ₓTeₓ)₅ thin films are nearly in good agreement and confirms the formation of MoBi₂Se₅, MoBi₂(Se₀.₅Te₀.₅)₅ and MoBi₂Te₅. Deviation from the atomic percentage of Mo⁴⁺, Bi³⁺, Se²⁻ and Te²⁻ could be due to the antisite defect [14, 15]. When we consider the position of chalcogenide in periodic table tellurium lies below selenium, also considering the value of Paulings electronegativity of Se (2.55), Te (2.1), Bi (2.02) and Mo (2.16) [16]. The reactivity of selenium is greater than tellurium due to difference in electronegativity, the amount of tellurium is observed less than selenium.

Figure 4.8 (a) shows a survey spectrum of the as deposited MoBi₂(Se₀.₂Te₀.₈)₅ thin films. It indicates that the binding energies of different states of the each elements present in the MoBi₂(Se₀.₂Te₀.₈)₅ thin films. Figure 4.8 (b) shows doublet observed at (Eb) 231.50 and 234.16 for corresponding core levels Mo 3d 5/2 and Mo 3d3/2. XPS spectra of Bi⁴f, figure 4.8 (c), shows doublet observed at binding energies (Eb) 165.35 and 170.64 for corresponding
core levels Bi 4f7/2 and Bi 4f5/2 respectively. Figure 4.8 (d) shows doublet at binding energy (Eb) 45.07 and 53.67 for corresponding core levels Se 3d5/2 and Se 3d3/2. Figure 4.8 (e) shows the doublet observed at binding energies (Eb) 574.12 and 585.07 for corresponding core levels Te 3d5/2 and Te 3d3/2. The approximate composition of the surface can be determined by dividing the individual peak area, after appropriate background subtraction, by their respective atomic sensitivity factor (ASF). For MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films deposited by APT the obtained ratio for approximate composition is 1:1.89:4.80.

Conductivity is important and gives reliable information about the transport phenomena and other physical properties of materials. Figure 4.9 shows plot of ln $\sigma$ vs 1000/T for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films having different compositions. It is clear that, the electrical conductivity of all samples under investigation increases linearly over the whole temperature range indicating normal semiconductor behavior of the MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. The linear variation of ln ($\sigma$) with 1000/T indicated that the conduction in these samples is through thermally activated process, which agrees well with the results of other workers for chalcogenide materials [17]. Activation energy of deposited films was calculated by equation discussed in Chapter II (section 2.11). Activation energies were found to decreases from 0.0321 to 0.0175 eV and conductivity increases from 1.0569 to 1.9548 (S cm$^{-1}$) as Te content increases in as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films which are listed in table 4.2. Moreover, it is evident that increase in the tellurium will leads to increase in conductivity and decrease in the activation energy for all compositions. This may be attributed to enhanced valence band tailing with incorporation of Tellurium and the different values of the electronegativity as well as the lattice parameters for both Se and Te atoms.

The TEP is defined as the ratio of thermally generated voltage to the temperature difference across a piece of semiconductor. The type of conductivity exhibited by the MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is determined from TEP measurement. Figure 4.10 illustrates the plot of Seebeck coefficient (S) vs
Temperature. The polarity of thermo emf shows positive sign towards hot end with respect to cold end, which confirms that MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are of n-type [11, 12, 17]. Most predominant carriers are electrons which may be due to the deficiency of Mo, Bi and the excess of Se and Te as shown by EDS.

Seebeck coefficient depends upon the location of fermi energy in the material and the type of scattering mechanism, the charge carriers encounter. It increases as the fermi energy shift towards conduction band. Moreover value of Seebeck coefficient increases more or less smoothly over the measured temperature region as Te increases. The negative values are observed only due to the n-type conduction. The Seebeck coefficient significantly enhanced (larger negative value for n-type thermoelectric semiconductor) from -80.5 to -188 $\mu$V K$^{-1}$ at 300 K is observed for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.

TEP was used to evaluate the hall mobility and carrier concentrations using the equation which is discussed in Chapter II (2.12). The carrier concentrations were calculated by using the equation discussed in Chapter II (2.13). The plots of log n Vs 1000/T of the investigated samples of different compositions are shown in figure 4.11. The number of free carriers decreases markedly as the temperature increases. This behavior may be attributed to difference of electro negativity and atomic radii of both Te and Se content.

The mobility ($\mu$) of charge carrier is determined by the equation in Chapter II (2.14 and 2.15). Figure 4.12 shows plot of log $\mu$ vs 1000/T for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. From the graph it is found that the mobility increases as temperature increases. Although high mobility is desired in thermoelectric devices, this typically will increase the electrical part of thermal conductivity as well as because charge carriers will easily transport heat in addition to charge. Figure 4.13 shows plot of overlay of mobility and carrier concentration vs Te content. It is observed that the carrier concentration decreases as the mobility increases with increase in Te content for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.
Section B
Annealed MoBi$_2$(Te$_{1-x}$Se$_x$)$_5$ Thin Films

4.B.1 Introduction

In the present investigation annealing is critical for semiconductors, which can strongly influence electrical transport behavior. It has been reported that annealing has a positive effect on the TE properties of bismuth telluride based materials [18]. Carrier concentration is important in optimizing thermoelectric ZT. If carrier concentration is low, conductivity of the semiconductor is high. The annealing can be used to alter the defect concentration of the materials, thereby altering the carrier concentration [19]. However, the thermometric properties of bismuth telluride based materials are changed not only by the carrier concentration but also by grain size and grain orientation, this will also be altered during the annealing process. Up to now, a few efforts have been made to research annealing effects on the structural and electrical properties of Bi$_2$Te$_3$-based thin films [20], but there is still need for optimization of the annealing temperature. Annealing the samples to remove defects in crystal structure is common. Annealed samples exhibit an increase in Seebeck coefficient [21]. ZT however will increase due to the greater contribution from the Seebeck coefficient.

Thermal treatment is necessary for fabrication process of several kinds of optoelectronic devices and Photoelectron Chemical (PEC) cells. The role of annealing process is very important in achieving high performance device and large PEC cell efficiency [22,23]. Therefore, in order to improve TE properties and PEC of the thin films, annealing effect on the structural and electrical transport properties have been investigated.

The as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were annealed at constant temperature (473 K) in muffle furnace and then characterized by following different techniques.
4.B.2 Characterization of Annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films

4.B.2.1. Thickness Measurement

It is observed that, terminal thickness of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films ranges from 235 to 310 nm as listed in Table 4.3. It is clear that thickness decreases after annealing for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. When annealing treatment is carried out at higher temperature the film material evaporate, and the films thickness decreases.

4.B.2.2 UV-Visible Absorption Spectra

Analysis of optical absorption spectra in solids provides essential information about band structure and the band gap energy in both crystalline and amorphous materials. Plot of $(\alpha h \nu)^2$ vs Photon Energy ($h \nu$) for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films shown in figure 4.14.

![Figure 4.14 Plot of $(\alpha h \nu)^2$ vs Photon Energy ($h \nu$) for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films](image)

4.B.2.3 X-ray Diffraction (XRD)

X-ray diffraction (XRD) patterns give valuable information about the nature and structure of the samples. The XRD patterns for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.15.
Figure 4.15 XRD patterns for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

4.B.2.4 Scanning Electron Microscopy (SEM)

Surface morphology of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were carried out by using Scanning Electron Microscopy (SEM). The SEM images for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.16.
Figure 4.16 SEM images for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films
4.B.2.5 Energy Dispersive X-ray Spectroscopy (EDS)

The quantitative analysis of annealed MoBi$_2$(Se$_{0.5}$Te$_{0.5}$)$_5$ thin films was carried out by using Energy Dispersive X-ray Spectroscopy (EDS) technique to study stoichiometry of the films. The EDS pattern for annealed MoBi$_2$(Se$_{0.5}$Te$_{0.5}$)$_5$ thin film is shown in figure 4.17.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Expected At. %</th>
<th>Actual At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>12.50</td>
<td>11.25</td>
</tr>
<tr>
<td>Bi</td>
<td>25.00</td>
<td>29.40</td>
</tr>
<tr>
<td>Se</td>
<td>31.25</td>
<td>34.70</td>
</tr>
<tr>
<td>Te</td>
<td>31.25</td>
<td>24.65</td>
</tr>
</tbody>
</table>

Figure 4.17 EDS pattern for annealed MoBi$_2$(Se$_{0.5}$Te$_{0.5}$)$_5$ thin film

4.5.1.6 Electrical Conductivity (EC)

The measurements of EC of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were carried out in temperature range 300–500 K using standard DC two point probe method. Plots of ln $\sigma$ Vs 1000/T for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.18.

Figure 4.18 Plot of ln $\sigma$ vs 1000/T for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin film
4.B.2.7 Thermoelectric Power (TEP) Measurement

The type of conductivity of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were determined from TEP measurement. Plots of Seebeck coefficient ($S$) vs Temperature for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.19.

**Figure 4.19 Plots of Seebeck coefficient ($S$) vs Temperature for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films**

**Carrier Concentration**

The carrier concentration of charge carriers were calculated and plots of log $n$ vs 1000/T for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.20.

**Figure 4.20 Plot of log $n$ vs 1000/T for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films**
Mobility

The mobility of charge carriers were calculated and plot of $\log \mu$ vs $1000/T$ for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is shown in figure 4.21.

![Figure 4.21 Plot of $\log \mu$ vs $1000/T$ for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films](image)

Plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs Te content for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is shown in figure 4.22.

![Figure 4.22 Plot of overlay of mobility and carrier concentration vs Te content for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films](image)
Table 4.3 Observed variation of film thickness, crystallite size, band gap and activation energy for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample id</th>
<th>Film thickness (nm)</th>
<th>Crystallite Size (nm)</th>
<th>Band gap (eV)</th>
<th>Activation Energy (ΔE) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoBi$_2$Se$_5$</td>
<td>a’</td>
<td>235</td>
<td>24.5</td>
<td>1.62</td>
<td>0.0301</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.8}$Te$_{0.2}$)$_5$</td>
<td>b’</td>
<td>240</td>
<td>30.6</td>
<td>1.51</td>
<td>0.0295</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.5}$Te$_{0.5}$)$_5$</td>
<td>c’</td>
<td>247</td>
<td>36.7</td>
<td>1.40</td>
<td>0.0244</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.4}$Te$_{0.6}$)$_5$</td>
<td>d’</td>
<td>260</td>
<td>40.2</td>
<td>1.36</td>
<td>0.0236</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.3}$Te$_{0.7}$)$_5$</td>
<td>e’</td>
<td>276</td>
<td>42.7</td>
<td>1.30</td>
<td>0.0201</td>
</tr>
<tr>
<td>MoBi$<em>2$(Se$</em>{0.2}$Te$_{0.8}$)$_5$</td>
<td>f’</td>
<td>300</td>
<td>45.7</td>
<td>1.25</td>
<td>0.0199</td>
</tr>
<tr>
<td>MoBi$_2$Te$_5$</td>
<td>g’</td>
<td>310</td>
<td>49.8</td>
<td>1.16</td>
<td>0.0171</td>
</tr>
</tbody>
</table>

4.B.2.8 Results and Discussion

Thickness of annealed samples was measured by surface profilometer. The thickness of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films ranges from 235 to 310 nm which are listed in table 4.3. The relative thickness of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is lower than as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. When annealing treatment is carried out at higher temperature the film material evaporates and the film thickness decreases.

The optical behavior of a material is generally utilized to determine the optical constants. The plots of $(\alpha h\nu)^2$ vs Photon Energy ($h\nu$) for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.14. It is evident that $E_g$ decreases after annealing from 1.62 to 1.16 eV which are listed in table 4.3. In chalcogenide thin films reduction of optical band gap has been observed after annealing [24, 25]. This decrease in the $E_g$ after annealing can be interpreted in terms of inducing crystallization in semiconducting glasses. During annealing process, bond breaking and bond arrangement can take place, which result in change in local structure of thin films. These include superior effect such as shifts in the absorption edge, more substantial atomic and molecular reconfiguration which is associated with changes in optical constants and absorption edge shift. Consequently, crystallization via nucleation and growth become possible and depends on the annealing temperature. During the process of annealing, enough vibrational energy is present to break some weaker bonds thus introducing some translational degree of freedom to the system, which
results, increase in the heat capacity of the system and decrease in the optical band gap.

XRD pattern of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.15. The XRD result indicates that the thin films are polycrystalline and the diffraction peaks are sharpened by annealing temperature. The diffraction peaks for sample a’ are found at 26.45°, 29.42°, 43.76°, 47.59°, 53.26°, 57.80° and 72.20° corresponding to lattice planes (010), (221), (343), (105), (106), (112) and (116) respectively. For sample b’ to f’ the diffraction peaks becomes sharp and are found at 20 values 27.96°, 31.08°, 32.74°, 47.34°, 53.58°, 55.58° and 57.71° corresponding to planes (115), (107), (102), (105), (112), (110), (0210) respectively. The diffraction peaks for sample g’ are found at 25.05°, 27.67°, 29.35°, 40.33°, 43.64°, 47.83°, 53.63°, 63.00° and 71.65° degree for corresponding planes (004), (211), (101), (312), (105), (232), (112) and (1118) respectively. After annealing the material shows mixed phase formation i.e. rhombohedral and hexagonal crystal structure. Likewise the similar observation was found in the chalcogenide material by Huimin Jia [26]. For sample a’ peak positions were compared with standard peak positions in XRD patterns of Bi$_2$Se$_3$ and MoSe$_2$ binary systems with JCPDS cards no 85-0519 (rhombohedral) and 77-1715 (hexagonal) respectively. For samples b’ to f’ the peak positions were compared with Bi$_2$Te$_3$, Bi$_4$Se$_3$, MoTe$_2$ and MoSe$_2$ binary systems with JCPDS card no. 72-2036 (rhombohedral), 72-2065 (rhombohedral), 72-0117 (hexagonal) and 17-0887 (hexagonal) respectively. For sample g’ Bi$_2$Te$_3$ and MoTe$_2$ binary systems compared with JCPDS card no. 72-2036 (rhombohedral) and 72-0117 (hexagonal) respectively. From figure 4.15 (b’ to f’) it is clear that in all samples, (115) plane is a more intense peak with preferred orientation. When the MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were annealed at 473 K, diffusion and agglomeration of atoms were accelerated and then the thin films crystallization is improved. The intensity, c-axis perpendicular planes becomes stronger, which means the layered structure of MoTe$_2$, Bi$_2$Te$_3$, MoSe$_2$ and Bi$_2$Se$_3$ may be formed. The crystallite size increases from 24.5 to 49.8 nm after annealing for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films which is listed in table 4.3.
Figure 4.16 shows the surface morphology of annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. It reveals that after annealing, the fibrous reticulate porous framework does not get disturb but the thickness of the fibers and pore size decreases MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. For the last sample a well defined grain with increase in grain size was observed up to 420 nm. This may occur because the granular formation of crystallites and consequent coalescing at high temperature for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films.

The atomic percentage compositions of the annealed MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films were measured by EDS technique. Figure 4.17 shows EDS spectrum of the annealed MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin film. Inset of figure 4.17 gives the atomic percentage composition of the elements in the MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films which indicates that the thin films has near stoichiometric composition and decrease in atomic percentage of selenium and tellurium in the annealed thin films. This may be due to the loss of selenium and tellurium during annealing process. The loss of selenium and tellurium occurs in annealed thin films because atomic bonds are not equivalent in all the directions at the surface.

Electrical conductivity measurements were made in temperature range 300 to 500 K at constant voltage (5 V). The variation of ln $\sigma$ vs 1000/T for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.18. The measurement shows an increase in electrical conductivity of the materials with increase in temperature indicating all the films are semiconducting in nature. From graph it reveals that electrical conductivity increase after annealing. Activation energy values for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films indicate that it has tendency to decreases as the thickness increase and hence grain size and crystallite size also increases. This is explained on the basis of Seto’s model [27] of polycrystalline materials. In polycrystalline materials when electron travels from one region to one region to other, they have to cross the grain boundary surfaces. Generally, a space charge region is built up at the grain boundary surfaces, creating a grain boundary potential. Hence electrons have to surmount this potential. The grain boundary potential should decreases as the
thickness increase and hence the grain size and crystallite size also increases. The energy required to surmount this grain boundary potential is called activation energy. From the slope of linear plots, activation energies were calculated and listed in table 4.3. The increase of electrical conductivity after annealing is mainly due to the preferred crystal orientation and the reduction of carrier scattering by grain boundaries. The increase in conductivity after annealing could be attributed to the larger grain size, which indicates that the film crystallinity is improved.

The Seebeck coefficient (S) vs Temperature for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.19. TEP were made using the integral method in which one end of the film was heated and the other kept at the constant low temperature and developed thermal electromotive force was measured with respect to the temperature gradient. All the samples show negative polarity of the generated voltage. This confirms n-type conduction of samples [28, 29]. From the figure it reveals that after annealing Seebeck coefficient for all the samples significantly increases (larger negative value for n-type thermoelectric semiconductor) which is listed in table 4.3.

The plots of log $n$ vs 1000/T of the annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are shown in figure 4.20. The number of carrier concentration of charge carriers decreases markedly as the temperature increases. Figure 4.21 shows plot of log $\mu$ vs 1000/T for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. It is found that the mobility of charge carriers increases with increases in temperature. Figure 4.22 shows plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs Te content. It is observed that the carrier concentration of charge carriers decreases as the mobility increases with increase in Te content for annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. This behavior may be attributed to difference of electro negativity and atomic radii of both Te and Se content.
Section C

Surfactant Assisted MoBi$_2$(Te$_{0.2}$Se$_{0.8}$)$_5$ Thin Films

4.C.1 Introduction

The addition of organic surfactants in the precursor solution is extremely important due to their influence on morphological and structural properties. The chemical structure of TOPO is responsible for its particular properties, due to presence of phosphine group (P=O). It acts as a surface active amphiphilic molecule containing hydrophilic head and hydrophobic tail. It contains lone pair of electron which is being used for formation of complex with metal ions, separation and purification of metals which is also applicable in preparation of high quality microstructures [30,31]. Many authors report that, the synthesis of nanocrystals with controllable size by applying Sodium Dodecyl Sulphate (SDS) and Tri-n-Octyl Phosphine Oxide (TOPO) surfactant due to its ability to control size and enhance particle stability [32-35]. In the present investigation we have studied the effect of surfactant viz. SDS and TOPO, on optostructural, morphological and electrical properties of MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films. MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films show better TE and slight enhancement in PEC properties therefore the effect of surfactant was undertaken for study on same composition.

The experimental set up for surfactant assisted synthesized MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films is same as that discussed in chapter III (section 3.2). For the synthesis of MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films 4 ml Mo-TEA, 16 ml Bi-TEA, 12 ml Sodium selenosulphide, 18 ml sodium tellurosulphide and 0.5 ml 5% SDS or 0.5 ml 5% TOPO was used. The whole volume of solution was made 100 ml by using double distilled water. The pH of solution was adjusted to 9.5. So as to deposit MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films with different morphologies, we have used the surface directing agent SDS and TOPO. Surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films were prepared by using SDS and TOPO are abbreviated as f-SDS and f-TOPO respectively. Optimized preparative parameters are summarized in table 4.4.
Table 4.4 Bath composition and optimized preparative parameters for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Film composition</th>
<th>Bath composition</th>
<th>Optimized Preparative parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>f-SDS</td>
<td>MoBi$<em>2$(Se$</em>{0.2}$Te$_{0.8}$)$_5$ with SDS</td>
<td>4 ml Mo-TEA + 16 ml Bi-TEA + 12 ml 0.25 M Na$_2$SeSO$_3$ + 18 ml 0.25 M Na$_2$TeSO$_3$ 0.5 ml of 0.5% SDS or 0.5 ml of 0.5% TOPO + double distilled water to make total volume 100 ml.</td>
<td>pH = 9.5 ± 0.2 Temperature = 55± 0.5 °C Deposition time = 3 hours Substrate rotation = 45 ± 5 rpm</td>
</tr>
<tr>
<td>f-TOPO</td>
<td>MoBi$<em>2$(Se$</em>{0.2}$Te$_{0.8}$)$_5$ with TOPO</td>
<td>4 ml Mo-TEA + 16 ml Bi-TEA + 12 ml 0.25 M Na$_2$SeSO$_3$ + 18 ml 0.25 M Na$_2$TeSO$_3$ 0.5 ml of 0.5% SDS or 0.5 ml of 0.5% TOPO + double distilled water to make total volume 100 ml.</td>
<td></td>
</tr>
</tbody>
</table>

4.C.2 Characterization of Surfactant Assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ Thin Films

4.C.2.1 Thickness Measurement

Terminal thickness of surfactant assisted MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films is 304 and 302 nm for f-SDS and f-TOPO respectively.

4.C.2.2 UV-Visible Absorption Spectra

The optical absorption studies were carried out mainly to determine optical band gap value of material under investigation. Optical absorption studies were carried out in the wavelength range 300 to 800 nm. Plots of $(ahv)^2$ vs Photon Energy (hv) for the surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films are shown in figure 4.23.
4.C.2.3 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) studies are generally carried out to determine the crystal structure of solid state material, either nanocrystalline, polycrystalline or amorphous. The XRD patterns for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films are shown in figure 4.24.

Figure 4.24 XRD patterns for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films
4.C.2.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopic (SEM) studies were carried out to determine surface morphology of thin film. The SEM micrographs for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films are shown in figure 4.25.

![SEM images for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films](image)

**Figure 4.25 SEM images for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films**

4.C.2.5 Electrical Conductivity (EC)

The measurements of EC of surfactant assisted MoBi$_2$(Te$_{0.2}$Se$_{0.8}$)$_5$ thin films were carried out in temperature range 300 – 500 K using standard DC two point probe method. Plots of $\ln \sigma$ Vs 1000/T for surfactant assisted MoBi$_2$(Te$_{0.2}$Se$_{0.8}$)$_5$ thin film are shown in figure 4.26.

![Plots of $\ln \sigma$ vs 1000/T for surfactant assisted MoBi$_2$(Te$_{0.2}$Se$_{0.8}$)$_5$ thin films](image)

**Figure 4.26 Plots of $\ln \sigma$ vs 1000/T for surfactant assisted MoBi$_2$(Te$_{0.2}$Se$_{0.8}$)$_5$ thin films**
4.C.2.6 Thermoelectric Power (TEP) Measurement

Thermoelectric properties of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were measured in the temperature range 300 to 500 K. Plots of Seebeck coefficient (S) vs Temperature for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films are shown figure 4.27.

![Figure 4.27 Plots of Seebeck coefficient (S) vs Temperature for surfactant assisted MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films](image)

**Carrier Concentration and Mobility**

Plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs 1000/T is as shown in figure 4.28 for f–TOPO MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films.

![Figure 4.28 Plot of overlay of mobility and carrier concentration vs 1000/T for f-TOPO MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin film](image)
Plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs 1000/T is as shown in figure 4.29 for f-SDS MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films.

![Plot overlay mobility vs 1000/T](image_url)

**Figure 4.29** Plot of overlay of mobility of charge carriers and carrier concentration of charge carriers vs 1000/T for f-SDS MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin film

**4.C.2.7 Results and Discussion**

The fundamental absorption which corresponds to the electron excitation from the valence band to the conduction band can be used to determine value of optical band gap energy. Figure 4.23 shows plots of $(\alpha h\nu)^2$ vs Photon Energy $(h\nu)$ for the surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films. The nature of plots suggests that material posses direct allowed transition. After addition of surfactant the band gap energy increases than the as deposited MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films. This may be due to change in the nucleation process and growth kinetics in the presence of surfactant [36]. In the surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films f-SDS exhibit band gap energy 1.51 eV and for f-TOPO it is 1.62 eV because smaller nanoparticles deposited on substrate [37]. This variation in band gap within these two surfactants may be related with the crystallite size. In semiconductor nanoparticles the effective band gap energy increases with decrease in crystallite size and the absorption edge is blue shifted called as quantum size effect. The blue shift in the absorption edge is due to decrease in crystallite size caused using TOPO.
Figure 4.24 shows XRD pattern for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films. The diffraction peaks for f-SDS and f-TOPO thin films are found at 27.68°, 29.33°, 32.16°, 40.32°, 43.65° and 53.46° corresponding to lattice planes (015), (113), (012), (312), (1016) and (413) respectively. The plane indices are obtained by comparing the intensity and position of peaks with these of Bi$_2$Te$_3$, Bi$_2$Se$_3$, MoTe$_2$ and MoSe$_2$ binary systems which are given by JCPDS card no. 08-0027, 72-2123, 23-1257, 72-1420 respectively. The XRD patterns reveals that MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films exhibit rhombohedral crystal structure. In the presence of SDS the sharp peaks are observed and in the presence of TOPO the broad peaks are observed. The presence of broad XRD peak is an indication of nanocrystalline nature of the films [38, 39]. This shows that crystallites formed in case of f-SDS have larger size than in case of f-TOPO. The crystallite size for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films, f-SDS and f-TOPO is 29.2 and 25.1 nm respectively.

Figure 4.25 shows SEM for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films at (×10000) magnification. After addition of SDS in chemical bath during deposition of MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$, the old fibrous reticulate porous structure disturbed and fused together to form the particles of irregular shape which is shown in figure 4.25 (f-SDS). SDS is a peculiar surfactant which acts like a template and catalyzed the self assembled growth of lamellar nanostructures [40]. After addition of TOPO in chemical bath during deposition of MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$, uniform fibrous sheet with randomly distributed rods was observed which is shown in figure 4.25 (f-TOPO). Such behavior is observed in the presence of TOPO with longer chain generates smaller particles due to the slower nucleation and growth rate [41]. In the presence of TOPO nucleation starts slowly because strong binding of the TOPO with surface nanoparticle therefore it shows more compact fibrous sheet like structure.

The electrical conductivity of surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin film were measured using dc two probe method. The electrical conductivity were found to be a function of temperature range 300-500 K. Plot of ln $\sigma$ Vs
1000/T is shown in figure 4.26 for surfactant assisted \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin film. An increase in conductivity with increase in temperature confirms that surfactant assisted \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin films are semiconductor in nature. From figure 4.26 it is observed that the surfactant assisted \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin films possesses high conductivity than the as deposited \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin film. The increase in conductivity is may be due to increase in particle size of surfactant assisted \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin films. The effect of size on the electrical conductivity of nanostructures is based on the following mechanisms: surface scattering, quantized conduction, coulomb charging and tunneling, widening and discrete band gap and change of microstructure. So increase in conductivity of surfactant assisted \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin films may be due to the decrease in grain boundary scattering, structural defects, dislocations and improvement in nanoparticle size [42]. From the slopes of the linear plots, activation energies were calculated. The activation energy for f-SDS and f-TOPO are 0.185 and 0.190 eV respectively.

In TEP measurements, the open circuit thermovoltage generated by the sample when a temperature gradient is applied across a length of the sample was measured using digital micro voltmeter. The temperature difference between the hot ends of the samples causes transport of carriers from hot to cold end, thus creating an electric field, which gives rise to thermovoltage across the ends. The thermovoltage generated is directly proportional to temperature gradient maintained across the semiconductor ends. From the sign of the multimeter terminal connected at the cold end, one can deduce the sign of predominant charge carriers. Figure 4.27 shows a plot of Seebeck coefficient (S) vs Temperature for \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin films. In case of surfactant assisted \( \text{MoBi}_2(\text{Se}_{0.2}\text{Te}_{0.8})_5 \) thin films the negative terminal was connected to cold end, therefore the film shows n-type conductivity and Seebeck coefficient also shows the negative sign which confirms the n-type conduction mechanism [17]. The Seebeck coefficient for f-SDS and f-TOPO are -192 and -220 \( \mu \text{V} \text{K}^{-1} \) at 300 K respectively. The plots of overlay of mobility of charge carriers and carrier concentration of charge carriers vs 1000/T of surfactant assisted f-
TOPO and f-SDS thin films are shown in figure 4.28 and 4.29 respectively. From the graphs it is observed that the carrier concentration decreases as the mobility increases for both surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films.

**4.D Conclusion**

Nearly stoichiometric MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films were prepared by APT. The surfactant assisted f-SDS and f-TOPO thin films are also prepared by APT. Band gap energies were found to decrease from 1.78 to 1.44 eV as Te content and thickness increases in as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. After annealing the band gap decreases from 1.62 to 1.16 eV for MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. The surfactant assisted f-SDS and f-TOPO thin films exhibit band gap 1.51 and 1.62 eV respectively. X ray diffraction pattern of the as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ films and surfactant assisted f-SDS and f-TOPO thin films shows the formation of nanocrystalline thin film with rhombohedral crystal structure. After annealing of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films rhombohedral and hexagonal mixed phase was obtained. It reveals that for as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films, the crystallite size increases from 20.8 to 38.4 nm as the Te content increases in MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films. After annealing of MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films the crystallite size increases from 24.8 to 49.8 nm also for surfactant assisted MoBi$_2$(Se$_{0.2}$Te$_{0.8}$)$_5$ thin films the crystallite size decreases than as deposited thin films, it exhibits 29.2 and 25.1 nm respectively. From the EDS and XPS it reveals that, stoichiometric films with well defined composition have been obtained for selected samples. The as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are fibrous reticulate porous framework in nature. After annealing the fibrous reticulate porous framework does not get disturbed but thickness of the fibers and pore size increases. After addition of surfactants such as SDS and TOPO the different morphologies were observed. The AFM and TEM images of as deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ thin films are resembles with the corresponding SEM images. From electrical properties it reveals that these films are semiconductors with n-type conduction.
Synthesis and Characterization of $\text{MoBi}_2(\text{Te}_{1-x}\text{Se}_x)_5$ Thin Films

References


[16] N. Greenwood and A. Earnshaw, Chemistry of Element 1st eds. Pergaman


### Content

**Section A**
As Deposited MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films

<table>
<thead>
<tr>
<th>4.A.1 Introduction</th>
<th>137</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.A.2 Experimental Details for Deposition of MoBi$<em>2$(Se$</em>{1-x}$Te$_x$)$_5$ Thin Film</td>
<td>138</td>
</tr>
<tr>
<td>4.A.3 Mechanism of MoBi$<em>2$(Se$</em>{1-x}$Te$_x$)$_5$ Thin Film Formation</td>
<td>139</td>
</tr>
<tr>
<td>4.A.4 Characterization of As Deposited Quaternary MoBi$<em>2$(Se$</em>{1-x}$Te$_x$)$_5$ Thin Films</td>
<td>141</td>
</tr>
<tr>
<td>4.A.4.1 Thickness Measurement</td>
<td></td>
</tr>
<tr>
<td>4.A.4.2 UV-Visible Absorption Spectra</td>
<td></td>
</tr>
<tr>
<td>4.A.4.3 X-ray Diffraction (XRD)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.4 Scanning Electron Microscopy (SEM)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.5 Atomic Force Microscopy (AFM)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.6 Transmission Electron Microscopy (TEM)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.7 Energy Dispersive Spectroscopy (EDS)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.8 X-ray Photoelectron Spectroscopy (XPS)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.9 Electrical Conductivity (EC)</td>
<td></td>
</tr>
<tr>
<td>4.A.4.10 Thermoelectric Power (TEP) Measurement</td>
<td></td>
</tr>
<tr>
<td>4.A.4.11 Results and Discussion</td>
<td></td>
</tr>
</tbody>
</table>

**Section B**
Annealed MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films

<table>
<thead>
<tr>
<th>4.B.1 Introduction</th>
<th>156</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.B.2 Characterization of Annealed MoBi$<em>2$(Se$</em>{1-x}$Te$_x$)$_5$ Thin Films</td>
<td>157</td>
</tr>
<tr>
<td>4.B.2.1 Thickness Measurement</td>
<td></td>
</tr>
<tr>
<td>4.B.2.2 UV-Visible Absorption Spectra</td>
<td></td>
</tr>
<tr>
<td>4.B.2.3 X-ray Diffraction (XRD)</td>
<td></td>
</tr>
<tr>
<td>4.B.2.4 Scanning Electron Microscopy (SEM)</td>
<td></td>
</tr>
<tr>
<td>4.B.2.5 Energy Dispersive Spectroscopy (EDS)</td>
<td></td>
</tr>
<tr>
<td>4.B.2.6 Electrical Conductivity (EC)</td>
<td></td>
</tr>
<tr>
<td>4.B.2.7 Thermoelectric Power (TEP) Measurement</td>
<td></td>
</tr>
<tr>
<td>4.B.2.8 Results and Discussion</td>
<td></td>
</tr>
</tbody>
</table>
Section C
Surfactant Assisted MoBi$_2$(Se$_{0.5}$Te$_{0.5}$)$_5$ Thin Films

4.C.1 Introduction 167

4.C.2 Characterization of Surfactant Assisted MoBi$_2$(Se$_{1-x}$Te$_x$)$_5$ Thin Films 168

  4.C.2.1 Thickness Measurement
  4.C.2.2 UV-Visible Absorption Spectra
  4.C.2.3 X-ray Diffraction (XRD)
  4.C.2.4 Scanning Electron Microscopy (SEM)
  4.C.2.5 Electrical Conductivity (EC)
  4.C.2.6 Thermoelectric Power (TEP) Measurement
  4.C.2.7 Results and Discussion

4.D Conclusion 175

References 176