CHAPTER 6

SINGLE PHASE AND ITS STABILITY
IN AgSbTe$_2$ FILMS

CONTENTS

6.1 Introduction 75
6.2 Experimental 76
6.3 Results and discussion 77
6.4 Conclusions 84
References 86
Figures
6.1 Introduction

It is seen in the preceding chapter that the direct thermal evaporation of AgSbTe$_2$ in vacuum yields a two phase (AgSbTe$_2$ + Ag$_2$Te) film inevitably. It has been attributed to the fractional loss of Sb$_2$Te$_3$ during the evaporation. Several workers in the past faced similar situations in vacuum deposition of various binary and ternary compounds. However, by adopting suitable compensation mechanisms single phase films could successfully be grown in most of the cases. For example, monophase InSb films were grown by recrystallization from the
liquid phase of a non-stoichiometric melt containing an excess of Sb\(^{1}\). Composite films of In and Sb were first deposited by co-evaporation of the elements from separate crucibles onto unheated glass or pyrex substrates. Optimum results were obtained with an In:Sb ratio of 1.273 (by weight). The excess Sb was required to compensate the fractional loss during the recrystallization. An addition of a small quantity of the more volatile group V component to the powdered source material was suggested even in the case of flash evaporation of III-V compounds\(^\text{2}\). In the case of certain ternary films annealing in active gases (e.g., \(\text{H}_2\text{S}\) for CuInS\(_2\) and \(\text{H}_2\text{Se}\) for CuInSe\(_2\)) was suggested to compensate for the sulphur and selenium deficiencies in these films\(^3,4\)). Such compensation has been made in the present case by adding suitable amounts of the binary compound Sb\(_2\)Te\(_3\) to the initial source material AgSbTe\(_2\). The present chapter describes, in detail, the experimental procedure and the results obtained during the preparation of single phase and homogeneous AgSbTe\(_2\) films.

6.2 Experimental

Two binary compounds, Ag\(_2\)Te and Sb\(_2\)Te\(_3\)
were used in the present investigation. These compounds were prepared by melting the stoichiometric amounts of pure individual elements in sealed quartz ampoules. The X-ray powder diffraction analysis confirmed the compound formation. Known amounts of \( \text{Sb}_2\text{Te}_3 \) were then mixed mechanically with stoichiometric starting material \( \text{AgSbTe}_2 \). The mixture was then carefully evaporated from tungsten boats onto various substrates. The other experimental details were essentially the same as those described in chapter 5.

6.3 Results and discussion

There are several conflicting reports regarding the formation of single phase and its composition in \( \text{AgSbTe}_2 \) bulk crystals. Although the composition was originally reported to be congruently melting and homogeneous at room temperature, later investigations reported that an intermediate phase forms by the ternary equivalent of peritectic reaction at 565°C and two phases persist at room temperature\(^5,6\). There is also a mention of eutectoid decomposition at 360°C\(^7\). It is not clear from the literature available why this composition does not yield a
homogeneous material. This behaviour has been attributed to one or more of the following reasons: non-equilibrium conditions, the existence of eutectoid transformation or the composition of the intermediate phase being different from $\text{AgSbTe}_2$. Astakhov et al.\cite{9} recently reported the single phase composition of $\text{AgSbTe}_2$ as $\text{Ag}_{0.82} \text{Sb}_{1.18} \text{Te}_{2.18}$, with 41 mole % $\text{Ag}_2\text{Te}$ and 59 mole % $\text{SbTe}_3$. Earlier to this, Stegherr et al\cite{10} reported the composition as $\text{Ag}_{19} \text{Sb}_{29} \text{Te}_{52}$. Burmeister and Stevenson\cite{8} reported the formation of single phase material with NaCl type structure with 59 mole % $\text{Sb}_2\text{Te}_3$ (balance $\text{Ag}_2\text{Te}$). The composition was found to be in a metastable state as prolonged annealing resulted in the precipitation of $\text{Sb}_2\text{Te}_3$ on the (111) planes of the ternary phase.

In the present work where thin films are concerned, the addition of a small amount of $\text{Sb}_2\text{Te}_3$ to the $\text{AgSbTe}_2$ evaporant has been found to bring considerable changes in the final film structure. Optimum results were obtained when a mixture of 70 mole % $\text{AgSbTe}_2$ and 30 mole % $\text{Sb}_2\text{Te}_3$ was evaporated. Figure 6.1 represents a series of electron diffraction patterns obtained when the mixture was evaporated and condensed.
dissociation was observed at about 200 °C whereas Pinsker and Imamov\textsuperscript{11} observed it at 100 °C. The composition of the ternary phase might be a factor for the discrepancy in the temperatures of stability. Exact determination of composition of the single phase could not be made. Diffraction patterns obtained from mixtures with greater than 40 to 50 mole % \( \text{Sb}_2\text{Te}_3 \) were found possessing extra lines.

As already mentioned, optimum results could be obtained with a mixture of 70 mole % \( \text{AgSbTe}_2 \) and 30 mole % \( \text{Sb}_2\text{Te}_3 \). This can be considered, approximately, equal to a binary mixture of 75 mole % \( \text{Sb}_2\text{Te}_3 \) and 25 mole % \( \text{Ag}_2\text{Te} \). Hence, a ternary phase should be formed when separate evaporations are made with the above concentrations. In actual practice, the ternary phase could easily be prepared by the method of inter-diffusion\textsuperscript{12,13} in thin film couples. Taking binary compounds \( \text{Ag}_2\text{Te} \) and \( \text{Sb}_2\text{Te}_3 \) separately in two tungsten boats, first a thin film of \( \text{Sb}_2\text{Te}_3 \) was deposited onto an unheated NaCl surface and was immediately followed by the second evaporation of \( \text{Ag}_2\text{Te} \). The total thickness was about 500 Å. When the film couple was annealed for 5 hours at about 100 °C
liquid phase of a non-stoichiometric melt containing an excess of Sb\textsuperscript{1}). Composite films of In and Sb were first deposited by co-evaporation of the elements from separate crucibles onto unheated glass or pyrex substrates. Optimum results were obtained with an In:Sb ratio of 1.273 (by weight). The excess Sb was required to compensate the fractional loss during the recrystallization. An addition of a small quantity of the more volatile group V component to the powdered source material was suggested even in the case of flash evaporation of III-V compounds\textsuperscript{2}). In the case of certain ternary films annealing in active gases (e.g., H\textsubscript{2}S for CuInS\textsubscript{2} and H\textsubscript{2}Se for CuInSe\textsubscript{2}) was suggested to compensate for the sulphur and selenium deficiencies in these films\textsuperscript{3,4}). Such compensation has been made in the present case by adding suitable amounts of the binary compound Sb\textsubscript{2}Te\textsubscript{3} to the initial source material AgSbTe\textsubscript{2}. The present chapter describes, in detail, the experimental procedure and the results obtained during the preparation of single phase and homogeneous AgSbTe\textsubscript{2} films.

6.2 Experimental

Two binary compounds, Ag\textsubscript{2}Te and Sb\textsubscript{2}Te\textsubscript{3}
the formation of the single phase ternary compound was completed (Fig. 6.2). The stability of the phase was found to be the same as that observed in the above cases. The d-spacings observed in different cases are summarized in Table 6.1 and compared with the calculated values.

Figure 6.3 demonstrates the grain growth with annealing temperature in the single phase films. At the low temperature the annealing resulted in a substantial increase in crystallite size (Fig. 6.3(b)). When the films were annealed at 200 °C for nearly 20 hours, partial decomposition and evaporation occurred (Fig. 6.3(c)) and corresponding extra phases appeared in the electron diffraction patterns.

A slight rise in the deposition temperature was found to have a disastrous effect on the stability of the single phase. The single phase AgSbTe₂ was found dissociating and leading to the formation of two phase (AgSbTe₂ + Ag₂Te) films irrespective of variations in the deposition parameters. Figure 6.4(a), thus, shows the selected
Table 6.1  d-spacing data for AgSbTe$_2$ films

<table>
<thead>
<tr>
<th>hkl</th>
<th>Calculated</th>
<th>Films on NaCl annealed at 200°C for 5 H</th>
<th>Film on C annealed at 200°C for 5 H</th>
<th>Sb$_2$Te$_3$-Ag$_2$Te film couple on NaCl annealed at 100°C for 5 H</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>3.509</td>
<td>3.489</td>
<td>3.491</td>
<td>3.490</td>
</tr>
<tr>
<td>200</td>
<td>3.039</td>
<td>3.067</td>
<td>3.033</td>
<td>3.035</td>
</tr>
<tr>
<td>220</td>
<td>2.149</td>
<td>2.153</td>
<td>2.132</td>
<td>2.148</td>
</tr>
<tr>
<td>311</td>
<td>1.833</td>
<td></td>
<td></td>
<td>1.825</td>
</tr>
<tr>
<td>222</td>
<td>1.755</td>
<td>1.772</td>
<td>1.731</td>
<td>1.756</td>
</tr>
<tr>
<td>400</td>
<td>1.520</td>
<td>1.523</td>
<td></td>
<td>1.518</td>
</tr>
<tr>
<td>331</td>
<td>1.394</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>420</td>
<td>1.359</td>
<td>1.363</td>
<td>1.329</td>
<td>1.350</td>
</tr>
<tr>
<td>422</td>
<td>1.241</td>
<td>1.241</td>
<td>1.251</td>
<td>1.230</td>
</tr>
<tr>
<td>333,511</td>
<td>1.170</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>440</td>
<td>1.074</td>
<td>1.074</td>
<td>1.067</td>
<td>1.066</td>
</tr>
<tr>
<td>531</td>
<td>1.027</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600,442</td>
<td>1.013</td>
<td>1.008</td>
<td></td>
<td>1.008</td>
</tr>
<tr>
<td>620</td>
<td>0.9610</td>
<td>0.9494</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*From Ref. 14.
are electron diffraction (SAED) pattern obtained when a mixture of 70 mole % AgSbTe$_2$ and 30 mole % Sb$_2$Te$_3$ was evaporated onto (100) surface of NaCl kept at 100 °C. The pattern demonstrates a mixed 2d - {100} + {111} orientation of the crystals and is clearly seen at still higher temperatures (Fig. 6.4(b)). The two spotty rings close to (220) reflection of AgSbTe$_2$ are due to the Ag$_2$Te phase. Even though the patterns appeared to be complex, a detailed consideration of the disposition of spots etc., showed the formation of a 2d - {100} + {111} orientation of the cubic AgSbTe$_2$ phase, but the crystallites were mutually rotated by 30°. Variation of composition, deposition rate and temperature failed to prevent the dissociation and formation of epitaxial growth of cubic AgSbTe$_2$ could not be observed. Similar results were obtained on other crystalline substrates, such as KCl, KBr and KI.

Deposits formed on carbon substrates (backed by NaCl surfaces) at room temperature (27 °C), from the mixture of Sb$_2$Te$_3$ and AgSbTe$_2$ were found to be amorphous in nature (Fig. 6.5(a)). However, an amorphous to polycrystalline transformation could be
obtained by treating the deposits with high intensity
electron beam (Fig. 6.5(b)) inside the electron
microscope, as it was observed in the case of
deposits formed by evaporating AgSbTe$_2$ alone
(chapter 5). The only difference is the formation of
single phase in the present case. No extra phases
could be observed. The deposits when annealed at 200 °C
for about 5 hours still exhibited the cubic
AgSbTe$_2$ single phase only (Fig. 6.6). The strong
tendency for a preferred (110) orientation can be
observed. Annealing at still higher temperatures
ultimately led to the dissociation of the AgSbTe$_2$
phase. Deposits formed at higher temperatures were
essentially polycrystalline without any preferred
orientation.

6.4 Conclusions

Single phase ternary thin films of
AgSbTe$_2$ can be obtained by direct thermal
evaporation. The starting material composition
has to be suitably adjusted to compensate the
loss of volatile constituents during the evaporation.
The single phase films are found to be stable up to a temperature of about 200°C above which they dissociate into the corresponding binary phases $Ag_2Te$ and $Sb_2Te_3$. High temperature deposition could not bring a complete parallel epitaxy on cleavage surfaces of alkali halides.
References


Electron diffraction patterns obtained when a mixture of 70 mole % $\text{Ag}_3\text{SbTe}_2$ and 30 mole % $\text{Sb}_2\text{Te}_3$ was evaporated on (100) surfaces of NaCl at room temperature.

a) unannealed film,
b) annealed at 100°C for 5 h,
c) annealed at 200°C for 5 h,
Fig. 6.1  Electron diffraction patterns obtained when a mixture of 70 mole % AgSbTe$_2$ and 30 mole % Sb$_2$Te$_3$ was evaporated on (100) surfaces of NaCl at room temperature.

d) annealed at 200°C for 20 h.

Fig. 6.2  Electron diffraction pattern obtained from the thin film couple Ag$_2$Te - Sb$_2$Te$_3$ formed on NaCl at room temperature (27°C) and annealed at 100°C for 5 h.
Fig. 6.1(d)

Fig. 6.2
Transmission electron micrographs of AgSbTe$_2$ single phase films formed on NaCl surfaces at room temperature by the evaporation of AgSbTe$_2$ and Sb$_2$Te$_3$ mixture.

a) unannealed
b) annealed at 100°C for 5 h
c) annealed at 200°C for 20 h

(X 108,000).
Fig. 6.4  Electron diffraction patterns obtained when the mixture of AgSbTe$_2$ and Sb$_2$Te$_3$ was evaporated on NaCl substrates kept at
a) 100 °C and
b) 150 °C.
Fig. 6.5 Transmission electron micrographs and the corresponding SAED patterns obtained when the mixture of AgSbTe$_2$ and Sb$_2$Te$_3$ was evaporated on carbon surfaces at 27°C.

a) before beam heating, and
b) after beam heating (X 108,000)

Fig. 6.6 Electron diffraction pattern obtained from the deposit formed on carbon at 27°C and annealed at 200°C for 5 h.