CHAPTER - 3

GROWTH OF SnSe AND SnSe$_2$

SINGLE CRYSTALS AND THIN FILMS
CHAPTER - III

SECTION - I

Growth of SnSe and SnSe₂ single crystals and thin films.

1. Introduction

Semiconductor crystals are the basic materials for fabrication of most of the electronic and optoelectronic devices. These crystals are used either as substrates for the growth of epitaxial layers or directly for electronic applications. The performance of many types of devices depend on the purity, perfection, and homogeneity of the bulk crystals. Therefore many years of research have gone into the study of lattice defect formation and elimination as well as into methods to reduce residual impurity concentration and to improve dopant homogenity. Furthermore a continuous trend towards the use of crystals of larger diameter is observed.

The elemental semiconductors at their melting point exhibit very low vapour pressure; e.g. Si: 10⁻⁶ mm of Hg and Ge: 10⁻⁹ mm of Hg[1]. In contrast, most compound semiconductors contain volatile constituents which rapidly evaporate from the melt if no special precaution is taken. Numerous special growth techniques have been developed to cope with this phenomenon. A common feature of all these techniques is that the growth takes place in a closed system.
either in a completely sealed set-up or by encapsulation of the melt. For the growth of III-V compounds, the most important methods are the Liquid encapsulated Czochralski (LEC) technique[2-6], the horizontal Bridgman technique[7-8] and magnetic Czochralski technique[9].

The most important methods for the bulk crystal growth of II-VI compounds are the horizontal Bridgman and vertical Bridgman-Stockbarger techniques[10-11]. In the latter technique the compound is melted in a vertically mounted sealed silica crucible or ampoule placed inside a vertical furnace (Figure 1). The furnace consists of two parts separated by a baffle. The upper part, furnace one is at a temperature above the melting point \( T_m \), while furnace two at \( T < T_m \). In this way a steep temperature gradient is created. The ampoule can be suspended as shown in Figure 3.1. For growth to take place, the melt is frozen from the lower tip of the crucible by moving it down through the temperature gradient. One can also solidify the melt in the upper direction by cooling down the furnace so that the freezing isotherm moves continuously from the bottom to the top of the ampoule (Vertical gradient freezing technique[7]). As solidification starts at the pointed tip of the crucible, usually only one crystal is formed initially, enabling a bulk single crystal to be grown when the conditions are properly chosen.
Figure 3.1  Temperature profile of the furnace
One of the advantages of the vertical Bridgman technique is that the required shape and dimensions of the crystal can easily be pre-determined by means of the crucible configuration. A major drawback of the technique is the fact that both the melt and crystal stay in close contact with the crucible wall during the crystallization. Furthermore, the cooling crystal can be subjected to stress due to the difference in thermal expansion of the crucible and crystal, particularly when the adhesion occurs. Therefore materials that expand on solidification such as GaAs, and GaP are difficult to grow by this technique.

Grag et al.[12] have grown single crystals of p-type SnSe by simplified Bridgman method. The grown crystals were approximately 3 cm long and 1.5 cm in diameter. Elkorashy et al.[13] and Valiukonis et al.[14] have grown these crystals by Bridgman method. Yu et al.[15] have grown large single crystals of SnSe about 1 cm long and 1 cm in diameter, by the close tube vapour transport technique. Domingo et al.[16] have grown SnSe$_2$ single crystals by iodine vapour transport method, for which temperatures of 500°C at the ingot position and 400°C in the region of crystal growth provided the best temperature gradient. The duration of growth period was varied from 2 to 72 hours in this method. These crystals have a cleavage plane parallel to growth axis. Bertand et al.[17] have also grown these crystals by vapour phase growth.
Albers et al.[18] studied the SnSe-SnSe₂ eutectic, p-n multilayer structure. They have discussed the conditions required to grow a two-phase p-n heterojunction from a eutectic melt from general principles. It is shown that the lamellar SnSe-SnSe₂ eutectic exhibits $10^3$ to $10^4$ p-n heterojunctions per cm and crystallographic relationship between the SnSe and SnSe₂ lamellae is reported. They also discussed a sample chemical vapour etching technique which enables the components of the eutectic to be identified.

Chattopadhyay et al.[19] studied structural transitions in SnSe by neutron diffraction in the temperature range 295-1000 K using a high temperature furnace. Accurate positional and thermal parameters have been obtained as a function of temperature both in the $\alpha$ and $\beta$ phases. These investigations indicate that $\alpha \rightarrow \beta$ phase transition in SnSe is of the second order displacive type and consists mainly of the continuous movement of Sn and Se atoms almost entirely along the [100] direction and suggests the soft mode behaviour of a zone boundary phonon of the $\beta$ phase.

In this chapter is reported the single crystal growth of SnSe and SnSe₂ both from melt by Bridgman-Stockbarger Technique. This technique is advantageous in that the temperature gradient can be varied and its effect on crystal growth can be studied. The ampoule lowering rate is also varied.
These two important growing conditions were optimized by the author to obtain reasonably good crystals of SnSe and SnSe$_2$. A dislocation etchant to assess the perfection of SnSe crystals have been developed and the results are reported.

2. Experimental techniques

2.1 SnSe single crystals

Tin and selenium of 5N purity supplied by Nuclear fuel complex Hyderabad (60.05 wt. % of Sn and 39.95 wt. % of Se) were weighed to stoichiometric proportions, viz. up to a microgram using a microbalance and fused under a vacuum of $5 \times 10^{-5}$ torr in a quartz ampoule. This was put inside another quartz tube which was also sealed under vacuum ($5 \times 10^{-5}$ torr) because like GaAs and GaP, SnSe also expands during solidification. The outer jacket provides necessary vacuum protection for preventing oxidation of the sample while solidifying since usually the inner tube breaks when the temperature reduces around 500°C. The ampoule was kept at 950°C and rocked for 48 hours and cooled slowly to 500°C and kept at this temperature for about 20 hours more to complete the reaction. After this, the temperature of the furnace was slowly lowered to room temperature over 10 hours. This procedure produced fairly homogeneous compound.

The compound prepared as mentioned above was used for
growing single crystals by Bridgman-Stockbarger method. The ingot weighing 15 to 20 gms. was of about 3 to 4 cm long and with a diameter around 1.2 cm. It was kept at 950°C for 6 hours and lowered with a speed ranging from 4 mm to 10 mm/hour, through a temperature gradient ranging from 10°C/cm to 50°C/cm.

After various trials it was found that a temperature gradient of 15°C/cm and a lowering rate of 7 mm/hour were most suitable for SnSe single crystal growth. A typical temperature profile of the furnace is as shown in Figure 3.1.

Samples taken from different parts of the ingot were used to take X-ray powder diffractograms (Figure 3.2). The 'd' values calculated from the patterns and compared with A.S.T.M. values are given in Table 3.1. The samples were also used for EDAX measurements and found to contain Sn:Se in 1:1 atomic ratio with tolerable experimental errors.

The single crystalline character was checked by laue back reflection X-ray pattern of the cleavage plane (001). A typical pattern is shown in Figure 3.3. Apart from indicating that the sample is necessarily a single crystal, the sharpness of Laue spots show that the crystal is fairly perfect.
Figure 3.2 Representative X-ray diffractometer trace for bulk SnSe compound.
### Table 3.1

Observed 'd' spacing obtained by powder X-ray diffraction using copper Kα radiation for SnSe bulk and the calculated 'd' values using lattice parameters reported in the literature [39]

<table>
<thead>
<tr>
<th>(nkl)</th>
<th>d (Å) observed</th>
<th>d (Å) calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3.4930</td>
<td>3.5165</td>
</tr>
<tr>
<td>021</td>
<td>3.3510</td>
<td>3.3658</td>
</tr>
<tr>
<td>101</td>
<td>3.0278</td>
<td>3.0345</td>
</tr>
<tr>
<td>111</td>
<td>2.9308</td>
<td>2.9339</td>
</tr>
<tr>
<td>031</td>
<td>2.8488</td>
<td>2.8160</td>
</tr>
<tr>
<td>041</td>
<td>2.3676</td>
<td>2.3631</td>
</tr>
<tr>
<td>141</td>
<td>2.0803</td>
<td>2.0886</td>
</tr>
<tr>
<td>012</td>
<td>2.0359</td>
<td>2.0430</td>
</tr>
<tr>
<td>230</td>
<td>1.9255</td>
<td>1.9227</td>
</tr>
<tr>
<td>032</td>
<td>1.8241</td>
<td>1.8254</td>
</tr>
<tr>
<td>231</td>
<td>1.7586</td>
<td>1.7447</td>
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<td>340</td>
<td>1.7399</td>
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<td>132</td>
<td>1.6808</td>
<td>1.6886</td>
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<td>300</td>
<td>1.4838</td>
<td>1.4818</td>
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<tr>
<td>320</td>
<td>1.4388</td>
<td>1.4349</td>
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<tr>
<td>232</td>
<td>1.4078</td>
<td>1.4106</td>
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<td>321</td>
<td>1.3524</td>
<td>1.3562</td>
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<td>242</td>
<td>1.3357</td>
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<td>123</td>
<td>1.2960</td>
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</tr>
<tr>
<td>203</td>
<td>1.1750</td>
<td>1.1749</td>
</tr>
</tbody>
</table>
Microscopically the cleavage plane of the crystal was found to be fairly planar. The crystal size ranged from 3 to 4 cm with a diameter of around 1.2 cm. The growth axis was found to have an inclination of 45° to 60° with (001). In addition to Laue photograph, the features on oppositely matched cleavage surface (Figure 3.4) shows good one to one correspondence indicating the single crystallinity of the sample. The spots in the electron diffraction pattern are also quite sharp indicating that the sample is a single crystal.

In order to determine the dislocation density in the crystal, chemical etching technique was used. After several trials a new dislocation etchant capable of revealing sites of dislocation was developed. The etchant consists of saturated solution of iodine in methanol. Figure 3.5 shows etch patterns on oppositely matched cleavage faces etched for 15 seconds. There is an almost one to one correspondence between pits on two such faces, implying reliability of the dislocation etchant. The etchant produces well defined point bottomed rectangular etch pits at the sites of dislocations. The dislocation density of the crystal was found to be $10^4$ to $10^5$ cm$^{-2}$.

2.2 SnSe$_2$ Single Crystals

For preparing homogeneous compound SnSe$_2$, Sn and Se were mixed in 1:2 atomic ratio (42.91 wt% of Sn and 57.09% wt%
Fig. 3.3 Laue back reflection X-ray pattern of the cleavage plane (001) of SnSe single crystal

Fig. 3.4 Features on oppositely matched cleavage surfaces of SnSe single crystal (X 900)

Fig. 3.5 Etch pattern on oppositely matched cleavage surfaces of SnSe single crystal (X 900)
of Se) and sealed under vacuum (5 x 10 torr) in a quartz ampoule (25 cm in length and 1.2 cm in diameter). Mixing and homogenization were carried by the same method as used for SnSe. In this case the molten zone was provided by a temperature of 750°C (melting point 657°C). Powdered samples taken from different parts of the ingot were used for X-ray diffraction tests to confirm the formation of the homogeneous stoichiometric compound. Figure 3.6 shows X-ray powder diffraction pattern of SnSe$_2$, and the observed and calculated 'd' values are given in Table 3.2.

The homogeneous charge thus prepared was used to grow single crystals by Bridgman-Stockbarger technique. After various trials with different temperature gradients it was found that 15°C/cm is best suited and the ampoule lowering rate is 4 mm/hour. The temperature profile of the furnace is shown in Figure 3.1. After completion of lowering, the ampoule in the lower furnace was held at 400°C for 24 hours for annealing.

SnSe$_2$ crystal has a soft cleavage. The crystal size ranged from 20 mm x 12 mm (diameter) to 25 x 12 mm. The growth axis was found almost invariably to be perpendicular to [0001]. It is difficult to cleave the crystal with a blade because of the soft cleavage and the Laue back reflection photograph shows blurred spots indicating deformation of
Figure 3.6 Representative X-ray diffractometer trace for the bulk SnSe$_2$ compound.
TABLE - 3.2

Observed ‘d’ spacing obtained by powder X-ray diffraction using Copper Kα radiation and the calculated ‘d’ values using lattice parameters reported in the literature [39] for SnSe₂ bulk

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>d (Å) observed</th>
<th>d (Å) calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>6.150</td>
<td>6.14</td>
</tr>
<tr>
<td>101</td>
<td>2.900</td>
<td>2.91</td>
</tr>
<tr>
<td>003</td>
<td>2.040</td>
<td>2.04</td>
</tr>
<tr>
<td>110</td>
<td>1.902</td>
<td>1.91</td>
</tr>
<tr>
<td>004</td>
<td>1.534</td>
<td>1.54</td>
</tr>
</tbody>
</table>
the crystal while cleaving. The electron diffraction photograph taken for cellophane cleaved crystals show sharp spots (Figure 3.7) indicating that the sample is of good perfection.

SECTION - II

Preparation of thin films of SnSe and SnSe₂

1. Introduction

The achievement of growth of semiconducting crystalline films of large area on substrates of different materials is of technical importance to any solidstate device engineer. The heteroepitaxial composite structure is also of scientific interest because the epitaxy is determined by the special relationship between the atomic arrangement in the substrate and that of the atom in the appropriate crystallographic planes of the semiconducting films. The degree of crystalline perfection of the semiconducting deposits also depend largely upon the physical/chemical nature of the substrate surface.

It is quite well known that the nature of the substrate has great influence on the epitaxial growth of films, their structures, orientations and properties. The term 'epitaxy' which means 'arrangement on' was first introduced by Royer [20-21] to denote the phenomenon of oriented overgrowth of one crystal on the other. In his study of growth of
a number of crystals on different substrates, he observed that the atoms or ions of the deposit assumed an orientation in correspondence with the atomic arrangement of the substrate surface so that there is always a close fit between the two dimensional networks of the atoms of the substrate and the deposit. First oriented overgrowths were observed in the case of some minerals. Later on, with continued work in this area such overgrowths were observed in a large number of materials. Review of these can be found in the article of Wallerant [22] and Mugge [23].

On the basis of his works, Royer [20-21] put forward three rules of epitaxy. The chief among them is that when there exists a parallelism of lattice planes (one of the substrate and other of the deposit) which have identical or nearly identical atomic network and have similar lattice spacings, an oriented overgrowth can take place. The difference between the network spacing of the substrate surface and the deposit plane is generally expressed in terms of percentage misfit which can be defined by the expression (in percentage) 100(b-a)/a, where 'a' and 'b' represent the network spacings in the substrate and in the film, respectively. In the year 1949, Frank and Van der Merwe [24], treating the substrate as two dimensional network, theoretically derived the maximum limit to be 15% misfit permissible for the formation of the oriented overgrowth. However,
recent work on epitaxial growth (Goswami [25] Pashley [26] and others) which indicates that an oriented overgrowth can be obtained even when the misfit is large as 50%, questions the validity of the Van der Merwes' conclusions.

In the year 1952-53 Engel [27-28] proposed a theory for the oriented overgrowth of metals on salt substrates with an attempt to explain the observed fits and the epitaxial temperatures. She suggests that at the interface between the substrate and deposit, the metal gets ionized and a two dimensional chemical reaction takes place. Thus, a monolayer of the deposit-metal-salt gets formed at the substrate-deposit interface, and hence the orientation of the deposit should depend on the misfit of the intermediate metal salt lattice with both substrate and deposit lattices.

Eventhough during the last few decades many theories and explanations have been put forward about the oriented overgrowth, it is a fact that none of the existing theories are consistently general or applicable to all the cases. However, one fact becomes conclusive that the growth of the first few layers is governed by the substrate surface and hence it will be epitaxial (with respect to the substrate) and successive epitaxial growth will be controlled by the substrate-deposit pair, lattice fitting, substrate temperature, deposition rate, etc. It is probable that the orientation
of the first few layers would determine the final orientation of the overgrowth.

Extensive studies of the epitaxy of the elemental semiconductors (silicon and germinium) on sapphire ($\text{Al}_2\text{O}_3$) and spinel ($\text{MgAl}_2\text{O}_4$) substrates have been reported [29-32] in the last few years. These studies have led to a basic understanding of the silicon sapphire technology. Currently, the trend of development has extended to the III-V compound semiconductors. However, because of the complexity in material growth and device fabrication, development of IV-VI compounds on single crystalline substrate is still at an early stage. Now-a-days the attention of a number of leading laboratories in this field is diverted to the studies on epitaxial growth by new techniques, such as organometallic method [33-34] and a defect characterization of the composite materials. Several device substrates have been successfully fabricated in the heteroepitaxial systems with interesting results.

Marianio and Chopra [35] studied polymorphism in some IV-VI compounds induced by high pressure and thin film epitaxial growth. According to them, epitaxial growth on rock salt of thin films of normally orthorhombic ($\text{P}_{\text{nma}}$) $\text{SnS}$, and $\text{SnSe}$ and $\text{PbSnSe}_2$ induces $\text{NaCl}$ structures. There exists a close correlation between the lattice constants of the
corresponding NaCl and orthorhombic polymorphic structures of Pb and Sn compound.

Fernandez-Samuel et al. [36] conducted electron microscopic studies on phase transformation in thin films of Tin diselenide. According to them SnSe\textsubscript{2} is known to exhibit almost exclusively the 2H CdI\textsubscript{2} type structure in bulk (single crystal) form. He found that all as-deposited films are amorphous in nature and undergo an amorphous-crystalline transformation upon pulse annealing (200°C) the crystalline phase exhibiting the 2H bulk structure. Further pulse annealing at higher temperature (300 to 500°C) results in thermal decomposition of this 2H phase, giving rise to several other phases, namely SnSe, (orthorhombic) SnSe (Cubic) and Sn\textsubscript{2}Se\textsubscript{3} (tetragonal) phases, the SnSe phases exhibiting variations in lattice parameters. In addition a new incommensurate phase of SnSe has been obtained. A model is proposed for the formation of this phase from orthorhombic SnSe phase. The final product of decomposition was found to be tetragonal tin.

The main aim of the work presented in this section is to investigate the detailed structure of SnSe and SnSe\textsubscript{2}, thin films deposited on different substrates like glass and alkali halide crystals by using electron microscopy. Special attention is drawn to the crystallographic orientation and perfection of the films.
2. **Experimental**

The homogeneous compound prepared as mentioned above as use for preparing thin films. The unit used for evaporation was "Hind Hivac Vacuum Coating Unit-12A4" as described in Chapter-II. For evaporation of SnSe, the pressure was reduced to $10^{-5}$ torr. A molybdenum boat was used as the heating source. Freshly cleaved alkali halide crystals and glass slides were used as substrates. The substrates were kept 12 cm above source. The glass substrates were cleaned by ion bombardment and heated to 100°C to remove volatile contaminants if any.

3. **Results and Discussions**

3.1 SnSe thin films

3.1.1 **Characterization using X-rays**

X-ray diffractograms of the films deposited on glass substrates (thickness about 1000 Å) at various temperatures ranging from room temperature (30°C) to 200°C were taken. Typical diffractograms taken at 30°C and 200°C are shown in Figures 3.8(a) and 3.8(b) respectively. In both the cases the peak observed corresponds to (111) plane (indexed in terms of orthorhombic SnSe lattice). The comparative study of diffractograms clearly indicates that there is an increase in intensity of the peak for the film deposited at a substrate temperature of 200°C. This clearly indicates that the crystallinity of the film increases with substrate temp.
Figure 3.8 Typical X-ray diffractometer trace for SnSe thin films (a) deposited at 35°C and (b) (deposited at 200°C.)
Similar result have been reported by Dang Tran Quan in the case of SnSe thin films [37].

3.1.2 Characterization using Electron microscopy

Figure 3.9 shows the electron diffraction pattern and corresponding electron micrograph of the film deposited on air cleaved face (100) of NaCl crystal at room temperature (30°C). On analysis this pattern indicates that SnSe is grown epitaxially with a mixed structure of NaCl and orthorhombic types. The lattice parameter calculated from this pattern is $a = 5.99 \, \text{Å}$.

(a) Effect of annealing

The effect of annealing of the films grown at room temperature on NaCl cleavages was also studied in detail. For this study three temperatures were selected. Figures 3.10(a), 3.10(b), 3.10(c) show electron diffraction patterns and the corresponding electron micrographs of the films deposited at room temperature on air cleaved NaCl and annealed in vacuum at 100°C, 150°C and 200°C respectively. Figure 3.10(a) shows a dual pattern of simultaneously growing grains in different orientations, the difference in orientation being about 5 to 10° as implied by the pattern. This is so probably because the temperature was not high enough to reorient the grains in a single direction. All the above figures show fairly good spots. At the same time, there appears
Fig. 3.7  Electron diffraction pattern of SnSe$_2$
  single crystal

Fig. 3.9  Electron diffraction pattern and the corresponding electron micrograph of SnSe thin film deposited on air cleaved face (100) of NaCl crystal at room temperature (X 72,000)
Fig. 3.10 Electron diffraction patterns and the corresponding Electron micrographs of SnSe thin films deposited at room temperature and annealed at (a) 100°C (b) 150°C (c) 200°C (X 72,000)
forbidden odd reflections with low intensity. This may be because, the composition of the planes in the unit cell varies in an orderly manner and the scattering efficiency of these two different set of planes may not be the same and the electron beam would see two distinguishable types of planes, one with a spacing 'a' from the origin, i.e. \{100\} and other with a spacing 'a/2' from the origin, i.e. \{200\}. The \{001\} diffraction pattern will then be basically that of an f.c.c. structure as in Figure 3.11(c) but, in addition, the intermediate spots of the simple cubic pattern would appear with intensities determined by the difference in structure factors of the two elements, $F_{Sn} - F_{Se}$. Similar phenomenon is known to occur in the cases of Cu$_3$Au (f.c.c. system) and CsCl (b.c.c. system) [38], both of which have ordering of superlattice.

(b) **Effect of substrate temperature**

In order to study the epitaxial growth in detail, the films were deposited on (100) cleaved faces of NaCl crystal at a substrate temperature of 50, 100, 150 and 200°C. The electron diffraction pattern and the corresponding electron micrographs were then taken. Figure 3.11(a), 3.11(b), 3.11(c) show electron diffraction patterns of SnSe thin films on air cleaved NaCl substrates kept at 100°C, 150°C, 200°C respectively. In this case also, there is a systematic increase in grain size and spots are sharper with increase
Fig. 3.11 Electron diffraction pattern and the corresponding Electron micrograph of SnSe thin films deposited on NaCl substrates at substrate temperature (a) 100°C (b) 150°C (c) 200°C (X 72,000)
in substrate temperature indicating increasing crystallinity with substrate temperature. In the electron diffraction pattern with substrate temperature 200°C only even numbered reflections occur. The absence of orthorhombic structure and odd reflections of superlattice structure are a clear evidence of polymorphism occurring in SnSe films grown epitaxially on NaCl substrate at a temperature of 200°C.

(c) Structure of film grown on cleavage faces of KCl, NaBr, and KBr crystals

To study the effect of various substrate on epitaxial growth of SnSe thin films, the films were grown on (100) cleavage faces of KCl, NaBr and KBr at room temperature as substrate temperature. Figures 3.12(a), 3.12(b), 3.12(c) show the electron diffraction and electron micrograph of the films deposited on KCl, KBr and NaBr respectively. On analysis these patterns also indicate that SnSe is grown epitaxially with a mixed structure of orthorhombic and NaCl types. As in the case of the films on NaCl cleavages, here also forbidden odd reflection occur. The respective lattice parameters calculated from these patterns are listed in Table 3.3.

It is worthwhile to mention that the electron diffraction pattern of SnSe films deposited on KCl cleavages, exhibits dual diffraction spots due to overlapped grains as observed in the case of films deposited on NaCl cleavages (Figure
Fig. 3.12 Electron diffraction pattern and the corresponding Electron micrograph of SnSe thin films deposited at room temperature on (a) KCl (b) KBr (c) NaBr cleavages (X 72,000)
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5.99</td>
</tr>
<tr>
<td>KCl</td>
<td>5.86</td>
</tr>
<tr>
<td>KBr</td>
<td>5.88</td>
</tr>
<tr>
<td>NaBr</td>
<td>6.12</td>
</tr>
</tbody>
</table>

**TABLE - 3.3**

Lattice parameter of SnSe thin film deposited on various substrates
3.10(a)). Contrary to this the observed ring pattern in the case of films deposited on NaBr cleavages indicates polycrystalline nature of the film.

3.2 \textbf{SnSe}_2 \textbf{thin films}

\textit{SnSe}_2 \text{ thin films were also prepared using the same technique as for the SnSe film. The deposition rate was kept as 30 Å/sec.}

3.2.1 \underline{Characterization using X-rays}

X-ray diffractograms of the films deposited on glass substrates (thickness \(\sim 1000 \text{ Å}\)) at various temperatures ranging from room temperature (30°C) to 200°C were taken. Typical diffractogram taken at 200°C as substrate temperatures is shown in Figure 3.13. In the case of as-grown films there is no noticeable peak indicating amorphous nature of the film. For the films deposited at 200°C, the well defined peaks are obtained and can be indexed in terms of hexagonal \textit{SnSe}_2 lattice. In a polycrystalline film, the integrated intensity for (hkl) reflection is proportional to the volume of all crystallites that have their (hkl) planes parallel to the surface of the film. For a given specimen the values of relative integrated intensities of various (hkl) reflection are compared with standard values available from the ASTM data file, for randomly oriented powder.
Figure 3.13  Representative X-ray diffractometer trace for SnSe$_2$ thin film (substrate temperature 200°C)
The differences are usually ascribed to preferred orientation. In this case the peaks are almost same as in the bulk specimen indicating large grain size but no preferred orientation.

3.2.2 Characterization using electron microscopy

As in the case of SnSe thin films SnSe₂ films were deposited on air cleaved NaCl substrate at a reduced pressure of $10^{-5}$ torr. The electron diffraction pattern and corresponding electron micrographs were taken. Figure 3.14(a) shows the electron diffraction pattern and corresponding electron micrograph of the film deposited on $\{100\}$ face of NaCl substrate at room temperature. The diffused ring in electron diffraction pattern and no visible grains in electron micrograph indicate the amorphous nature of the film.

a. Effect of annealing

To study the effect of annealing, the films deposited on $\{100\}$ faces of NaCl cleavages at room temperature were annealed for three hours in vacuum at 50, 100 and 150°C respectively. The electron diffraction pattern and electron micrograph of these films were taken. Figures 3.14(b), 3.14(c), 3.14(d) show the electron diffraction pattern and the corresponding electron micrograph respectively of the films deposited on NaCl cleavages and annealed at 50, 100,
Fig. 3.14  Electron diffraction pattern and the corresponding Electron micrograph of SnSe$_2$ thin films deposited on NaCl cleavages at room temperature (a) and annealed at 50°C (b) (X 33,000)
Fig. 3.14 Electron diffraction pattern and the corresponding Electron micrograph of SnSe$_2$ thin film deposited at room temperature and annealed at (c) 100°C (d) 150°C (X 33,000)
Fig. 3.15  Electron diffraction patterns and the corresponding Electron micrographs of SnSe$_2$ thin film deposited on NaCl cleavages at a substrate temperature of (a) 50°C (b) 100°C (X 33,000)
Fig. 3.15  Electron diffraction pattern and the corresponding Electron micrographs of SnSe$_2$ thin films deposited on NaCl cleavages at a substrate temperature of (c) 150°C (d) 200°C (X 33,000)
150°C. There is systematic increase in crystallinity up to 150°C. For films annealed at 150°C, the spots are well defined with an orientation of (001) and every spot could be indexed. The d values calculated using this pattern (Fig. 3.14(d)) with standard d values are given in Table 3.4. There is no noticeable difference in the diffraction pattern of the films annealed at 150°C and 200°C. Above 200°C there are additional spots indicating multiphase structure. This may be due to re-evaporation of selenium.

b. **Effect of substrate temperature**

In order to study the effect of substrate temperature on the structure of SnSe evaporated films, they were grown on 100 faces of NaCl cleavages at 50°C, 100°C, and 200°C as substrate temperature. The electron diffraction and electron micrograph of these films are shown in Figures 3.15(a), 3.15(b), 3.15(c), 3.15(d) respectively. These photographs indicate that the films grown up to 50°C as substrate temperature are amorphous in nature. The films grown above 50°C as substrate temperature are polycrystalline in nature. The sharpness and increase in number of rings show that the crystallinity is improving up to 200°C. The d values calculated using the above pattern (Fig. 3.15(d)) with standard d values are given in Table 3.5. As in the case of annealing above 200°C, multiphases such as SnSe, \( \text{Sn}_2\text{Se}_3 \) are appearing. This is because of re-evaporation of Se.

4. **Conclusions**

**Growth of single crystals**


**TABLE - 3.4**

Diffraction data for tin diselenide thin film deposited at room temperature and annealed at 150°C (Figure - 3.14(d))

<table>
<thead>
<tr>
<th>hkl</th>
<th>Standard data (Å)</th>
<th>Thin film (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.299</td>
<td>3.204</td>
</tr>
<tr>
<td>200</td>
<td>1.649</td>
<td>1.673</td>
</tr>
<tr>
<td>300</td>
<td>1.10</td>
<td>1.11</td>
</tr>
<tr>
<td>400</td>
<td>0.824</td>
<td>0.835</td>
</tr>
</tbody>
</table>
TABLE - 3.5

Diffraction data for tin diselenide thin film deposited at 200°C as substrate temperature (Figure - 3.15(d))

<table>
<thead>
<tr>
<th>hkl</th>
<th>Standard data (Å)</th>
<th>Thin film (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>2.91</td>
<td>3.101</td>
</tr>
<tr>
<td>102</td>
<td>2.25</td>
<td>2.280</td>
</tr>
<tr>
<td>003</td>
<td>2.05</td>
<td>2.062</td>
</tr>
<tr>
<td>200</td>
<td>1.649</td>
<td>1.635</td>
</tr>
<tr>
<td>202</td>
<td>1.45</td>
<td>1.432</td>
</tr>
<tr>
<td>114</td>
<td>1.19</td>
<td>1.187</td>
</tr>
</tbody>
</table>
(1) Reasonably perfect SnSe single crystals about 3 to 4 cm in length and 1.2 cm in diameter can be grown using Bridgman-Stockbarger technique.

(2) SnSe₂ single crystals about 2 to 2.5 cm in length and 1.2 cm in diameter can also be grown using Bridgman-Stockbarger technique.

SnSe thin film

(3) SnSe thin films can be grown on glass and alkali halide substrates by a simple evaporation technique at a reduced pressure of 10⁻⁵ torr.

(4) Films grown on glass substrate have a preferred orientation along <111> direction.

(5) The grain size of the films grown on glass substrate increases with substrate temperature upto 200°C.

(6) Films grown on alkali halide cleavages show epitaxial growth.

(7) The films grown at room temperature as substrate temperature show mixed structure of NaCl and orthorhombic (SnSe) structure.

(8) Film grown at 100°C as substrate temperature show dual diffraction spots indicating the overlapping of grains.
(9) Films grown at 200°C show only even reflection, as f.c.c. superlattice.

(10) The grain size of the film grown in NaCl cleavages increases with the substrate temperature.

(11) In the case of annealed films, also, crystallinity (sharpness of the spot) increases with annealing temperature up to 200°C.

(12) Films grown on KCl, KBr, and NaBr substrates also show epitaxial growth.

(13) On KBr cleavages the presence of dual spots indicates overlapping of grains.

(14) The rings of diffraction pattern of films grown on NaBr cleavages indicate polycrystalline nature of the film.

\(\text{SnSe}_2\) thin film

(15) In the case of \(\text{SnSe}_2\) thin films also stoichiometric homogenous films can be grown on glass and alkali halide crystals.

(16) Films grown on glass substrate are amorphous in nature and with annealing crystallinity increases but there is no preferred orientation.
(17) There is no epitaxial growth of SnSe$_2$ films on alkali halides upto 200°C as substrate temperature.

(18) Annealing of the films upto 150°C on NaCl cleavages at room temperature, show systematic increase in grain size and the electron diffraction pattern indicates the systematic change in the pattern from diffused rings to broken rings and finally well defined spots indicating the re-crystallization of the film.

(19) There is no noticeable difference between films annealed at 150°C and 200°C.

(20) Above 200°C, there are additional spots indicating multiphase structure.

(21) Films grown upto 50°C as substrate temperature are amorphous in nature.

(22) The films grown above 50°C are polycrystalline in nature and the crystallinity increases with substrate temperature.

(23) Films grown at a substrate temperature above 200°C show multiphases of SnSe and Sn$_2$Se$_3$. 
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