Chapter 3

GROWTH PROCESS OF LAYERED TUNGSTEN DISELENIDE

1. Introduction

Since the early sixties a group of materials called the transition metal chalcogenide have received a rapidly growing interest. Of the sixty compounds of this family, about two-thirds assume layer structures. These MX₂ compounds (X = S, Se or Te) form a structurally and chemically well defined family. The basic structure of loosely coupled X-M-X sheets makes such materials extremely interesting. Within a layer the bonds are strong, while between adjacent layers they are remarkably weak. As a consequence the crystals have facile basic cleavage, lubricate and marked anisotropic in many physical properties which accounts for the great interest in this family of materials. Electrically, however they cover a wide spectrum of properties. They are insulators like HfS₂, semiconductors like Mo S₂, semi-metals like W Te₂ and Tc S₂ and true metals like Nb S₂ and VS₂. All the Nb X₂ and Ta X₂ are superconductors and the true metallic ones also show band antiferromagnetism below about 150 K [1]. The diversity of properties arises through the existence of non-bonding d-bands which are quite wide (1 eV) in these compounds and the degree to which they are filled. Some of the compounds like TaTe₂, Tc S₂ and ReSe₂ shows structural distortion which seems to make their properties different from other members. The anisotropy in chemical behavior has also attracted attention: particularly important have been discoveries that may atoms and molecules can be inserted between the adjacent layers, thus forming intercalation compounds [2-7].
The group VI compounds seem to possess only limited range of homogeneity: they can usually be prepared stoichiometrically and as single phase compounds. The difficulty, however, lies in the preparation of large single crystals. For the preparation of single crystals, the discovery of Chemical Vapour Transport technique [8] has been of great influence. It enabled investigators to grow single crystals of substances hitherto known as "difficult materials". The preparation of single crystals from the vapour phase has been described by Shafer and co-workers [9] and Nitsche [10]. Al-Hilli and Evans [11] directed their effort to transport some MX₂ compounds without using halogen and obtained crystals superior to those grown with bromine or iodine as an agent. In the direct vapour transport the free flowing black powder was distributed along the length of the tube and then heat treated for about two weeks. The authors [11] also emphasize the fact that the position of the ampoule in the temperature profile and the profile itself are very important. It is necessary to keep the temperature between the hot and cold zone within a particular temperature gradient, otherwise there will be no yield.

Tungsten diselenide is a semiconducting compound with relatively low electrical conductivity increasing with temperature. In the system W-Se -- extensively studied by Hick's [12] -- no evidence was found for existence of WSe₃, mentioned by Hansen [13], nor could selenides of tungsten lower than WSe₂ be detected. Investigation concerning the stoichiometry of WS₂ have indicated that the homogeneity range of this compound must be extremely narrow. The structure of diselenide is such that the metal atom trigonal prismatically surrounded by selenium [14] as in figure( 3.1). It seems that the only known modification of WSe₂ is the 2H-type (fig. 3.2) and no rhombohedral diselenide exists.
Figure 3.1 The crystal structure of 2H- MX₂

Figure 3.2 2H - Polypeptide structure
2. Practical aspects of crystal growth by Chemical Vapour Transport technique

The requisites for growth of crystals from chemical vapour transport are:
1. Two zone tubular furnace
2. Ampoules
3. Temperature sensors
4. Temperature controllers and recorders
5. Pure chemicals
6. High vacuum system
7. Cleaning of the ampoule
8. Careful loading of the transporting agent and feed materials

3. Furnace Design

Detailed description of laboratory and industrial furnaces may be found in the books of Otto [15] and Brice [16]. Figure (3.3) shows the schematic diagram of the furnace with temperature controller circuitry. The temperature of the two zones are separately controlled by this electronic circuitry.

The two zone horizontal or vertical furnace was used having a length of 60 cm and diameter 50 cm. This furnace can give maximum temperature of 1200°C for each zone with a power rating of 1.75 KVA using single phase supply. Kanthal wire (A1 grade, max. working temperature 1150°C) was used as heating element. Thermal insulation is achieved by using ceramic materials and their properties are well known. Sillimanite tube is selected as heating cavity. Mullite and ceramic wool were used to cover the sillimanite tube thereby giving an excellent thermal capacity. Kanthal wire was wound on the sillimanite tube equidistantly to ensure the constancy of the temperature for short distances. The separation between the zones imparts a
Figure 3.3 Schematic diagram of the furnace with temperature controller circuitry.
'dip' in the temperature profiles shown in figure (3.4). As the thermoelectric thermometry is more economical and offer precise measurements, thermocouples are used as temperature sensors.

4. Temperature measuring devices

In the chemical vapour transport growth the most common temperature measurement and control techniques are based on thermocouples. Since the thermoelectric power of variety of metals and alloy combinations are known, the temperature of one junction can be determined provided the other junction has the known temperature preferably ice point. According to Shenker et al [17] chromel-alumel thermocouples are found suitable in the range of 1200°C. The essential requirements for this is the purity which should be 99.999% of the individual metal or alloy. An alumina sheath has to be provided to protect the thermocouple from volatile corrosive vapours and traces of H₂ and Co. The sensitivity of the thermocouple to a consider extent depends on its diameters. It was found 0.5 mm diameter thermocouple is quite optimum.

5. Dual temperature controller cum recorder

Two units of temperature controller cum recorders [18] were effectively used for setting the temperature of the two zones of the furnace. The output of the chromel-alumel thermocouples were calibrated to 0.04mV/°C and were fed directly to the compactor circuits. Generally these sensors will give a very weak signal and will be amplified to control the power input of the furnace. Since the weak signals obtained from the thermocouples are passed to the controllers, it must be carefully shielded. Otherwise stray voltage may be introduced by direct coupling or capacitative coupling. Extension wire used to connect thermocouple output to the controller must be prepared from alloys with similar thermoelectric characteristics. Such wires are referred to as compensating cables. However use of this
Figure 3.4 Temperature profiles

- $\Delta T = 50^\circ C$
- $\Delta T = 60^\circ C$
- $\Delta T = 70^\circ C$
- $\Delta T = 80^\circ C$
compensating cables only minimize the error, hence the length of the connecting wire should be as short as possible and also it must be in isothermal conditions.

The comparators built around IC 324 N and its associated circuitry is as follows. By adjusting the hysteresis loop of the comparators, using hysteresis voltage regulators one can control the set(ON) and reset(OFF) voltage for the relay switches. The voltage corresponding to the setting temperature had already been referenced by the comparator. The zone heating coils were connected to the mains through relay switches and thereby the temperature of the zones were controlled by the each comparator circuitry (fig. 3.3).

The analog signals from the thermocouples were converted to digital one with the A/D converter. A three and half digit single chip A/D converter IC 7107 (Intersil) having high accuracy was used. This A/D converter provides a built in seven segment decoder and driver. Thus by using four seven segment display this temperature recorders can record temperature up to maximum of 1200°C.

6. Ampoules

The ampoules may be made of any material which does not melt, soften or react appreciably with the species in the system at the operating temperature. At temperatures upto about 450°C pyrex glass is suitable in many systems. At higher temperatures silica is commonly used, but an alternative is alumino-silicates.

The effect of change in the shape of the growth end of the ampoule has been studied by many authors [19,20]. A rounded end usually results in a distribution of crystallites over several centimeters. A tapered, pointed end defines the cold region much better. Although crystals still form over much of the end section, it is usually possible to remove unwanted ones by reversing the temperature gradient until a single crystallite remains. However, it is found that when the temperature gradient is changed back, crystallites soon form again in exactly the same positions, indicating that these are active sites on the capsule wall with lower potentials for nucleation.
Next stage was to extend the end of the ampoule by a narrow tube. Nucleation takes place inside the tube in several places, and after a time the crystallites grow together. By the time the growing mass emerged into the capsule, it often happened that one crystal occupied the full width of the narrow tube, and this crystal continued to grow into the ampoule.

The final stage of the evolution was to provide crystallite or seed, rather than wait for nucleation. A convenient way of doing so is to trap a crystallite above constriction in the end of the ampoule and insert a stopper (which is sufficiently air tight) above it. Generally it is considered that a rounded end to the ampoule gives the lowest possibility of developing unwanted nuclei, assuming that there is initially just one nucleus centrally in the end of the ampoule [19]. Nucleation control in vapour growth is schematically shown in the figures (3.5a-3.5d).

7. Vacuum System

In order to avoid explosion of the reaction tube at the growth temperature due to excess vapour pressure and to bring up an easy access of transportation of the material from the source zone to deposition zone (as mean free path of the gaseous particles is greater than or comparable to the size of the ampoule at the lowest total pressure), it is essential to evacuate the reaction tube containing material to be transported, to a pressure less than $10^{-5}$ torr depending on the vapour pressure of the material at the growth conditions. An oil rotary pump can be used for attaining a vacuum of $10^{-3}$ torr or less. In order to achieve a vacuum of $10^{-5}$ torr or less, diffusion pump within oil rotary pump (Edwards) is used.

8. Ampoule Cleaning

Cleanliness of the ampoule is one of the most important aspects in the growth of crystals by chemical vapour transport method technique. If the ampoules are not cleaned properly, the impurities may get into the growing crystal and spoil its quality.
Figure 3.5a-3.5d  Nucleation control in vapour growth
completely. The procedure adopted for cleaning the ampoule is as follows: The quartz tubes are washed with commercial liquid soap or detergent powder at first. Then the ampoules are rinsed with double distilled water for more than ten times. They are then filled with 5N chromic acid and kept for more than 24 hours. After this period the chromic acid is completely poured out and the ampoules are cleaned in the ultrasonic bath with double distilled water. Then the ampoules are once again filled with ethyl alcohol and left for few hours in the ultrasonic bath. After this, the ethyl alcohol is poured out and the ampoules are kept in the hot chamber (temperature of about 60° C) for few hours and then taken for carrying out the experiment.

9. Loading of transporting agent and feed material

The material to be grown is taken in the well cleaned tube A (fig. 3.6) and it is evacuated while it is gently heated with a hand torch. Then the whole system is cooled under vacuum, section B is loaded with an amount of transporting agent (e.g. iodine) through stopper D and the whole apparatus is evacuated to a pressure less than 10⁻³ torr, while Dewar flask fitted with liquid is kept around B to prevent evaporation of volatile transporting agent. By cooling the reaction tube A with liquid air or freezing mixture and gently heating B, all the transporting agent is sublimed into reaction tube A which is sealed off at the constriction E.

10. Preparation of polycrystalline WSe₂

Several reports exist on the preparative conditions of WSe₂; Silverman’s high pressure- high temperature experiments (covering a very wide pressure- temperature profile, up to 70 k bar and 2400° C) gave only the hexagonal form. Wildervank’s work [21] and the studies of Al- Hilli et. al [11], Brixner [22,23], Kershaw et. al [24], Revolinsky et. al [25] and Hick’s [12] report the preparations of crystalline substance
Figure 3.6 The tube system used for filling the reaction ampoules with iodine
by direct reaction of elements in stoichiometric ratio. Table 1 gives the temperature range and time taken for the preparation of polycrystalline WSe₂ by various workers.

Table 1

Temperature range and time for the preparation of polycrystalline WSe₂

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Refiring Temperature (°C)</th>
<th>Time (hours)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>900 - 1000</td>
<td>Nil</td>
<td>168</td>
<td>22</td>
</tr>
<tr>
<td>600 - 700</td>
<td>Nil</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>600 - 700</td>
<td>1000 - 1200</td>
<td>10 - 15</td>
<td>24, 25</td>
</tr>
<tr>
<td>700 - 800</td>
<td>Nil</td>
<td>72</td>
<td>27</td>
</tr>
<tr>
<td>550</td>
<td>1000</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>600</td>
<td>800</td>
<td>96</td>
<td>26</td>
</tr>
</tbody>
</table>

In the present work 99.99% pure tungsten and selenium powders obtained from Merck were taken in stoichiometric proportions and were placed in transparent quartz ampoules which were etched and vacuum baked. Total charge used in each experiment was 10gms. The transporting agent iodine (1.2mg/cm³ of ampoule) was also placed in the quartz ampoule along with the powders. The ampoule was evacuated to a pressure of $10^{-5}$ torr using oil diffusion pump. Care was taken while evacuating so that the materials from the ampoule did not enter into the vacuum system. The evaporation inside the ampoule was prevented by dipping the lower end of the ampoule into the freezing mixture. The ampoule was sealed off at the constriction of 3mm in diameter (sealing unit is shown in fig. 3.7). The sealed ampoule was thoroughly shaken to ensure a proper mixing of the powders. The ampoules were placed inside a muffle furnace with powder distributed along the length of the ampoule. The temperature of the furnace was increased in steps of 50 °C.
from room temperature to a reaction temperature of 800 °C. Slow heating was necessary to avoid any possibility of explosion due to the exothermic reaction between the elements. After 48 hours of stable heating the ampoule was allowed to cool. At this stage a loose powder product resulted, having considerably greater volume than the reacting elements and, this compound was in the form of free flowing, shiny polycrystalline mass. Sealed capsules with and without transporting agent are used for chemical vapour transport (CVT) and direct vapour transport (DVT) respectively.

Hick's [12] derived a general rule for the solubility that for effective doping in WSe₂; doping element have an ionic radius close to the melt and it must come from an adjacent group of the periodic table. Here titanium is selected as dopant for the WSe₂ matrix. titanium powder of 99.99% purity is sealed along with the tungsten and selenium powders in the stoichiometry W₁₄ Ti₁ Se₂ (0.02<x<0.04) in a quartz ampoule. Since the growth of crystals (especially doped) by chemical vapour transport leads to a condemnation of the grown crystals by the transporting agents, it is always advisable to grow them by direct vapour transport technique, if possible[26]. So by avoiding transporting agents, the ampoule is placed in a muffle furnace of 800 °C. After 48 hours, the ampoule was allowed to cool. The resulted polycrystalline mass is well shakened and the ampoule is again placed in the muffle furnace having 900 °C for 24 hours for refiring. After 24 hours, the cooled ampoule was subjected to DVT.

11. Growth of doped and undoped WSe₂ using CVT and DVT

The polycrystalline powder was put along the length of the ampoule and the ampoule was placed in the two zone horizontal furnace (fig. 3.7) provided with appropriate temperature profiles. The temperature of the furnace was increased slowly in steps of 70° C/ hr. The temperature of the vapourization (Hot) and
Figure 3.7  Horizontal tubular furnace and sealing unit

Figure 3.7a
deposition zones were adjusted to the theoretically predicted values [27] of 900 °C and 810 °C respectively. The expected reaction at the hot zone is

\[ \text{WSe}_2 \text{(s)} + \text{I}_2 \text{(g)} \leftrightarrow \text{WI}_2 \text{(g)} + \text{Se}_2 \text{(v)} \]

The expected reaction at the deposition zone is

\[ \text{WI}_2 \text{(g)} + \text{Se}_2 \text{(v)} \leftrightarrow \text{WSe}_2 \text{(s)} + \text{I}_2 \text{(g)} \]

This can be clearly depicted by a cyclic diagram (fig. 3.8) which enable us the movement of vapour species inside the closed ampoule. The growth experiments have done by various workers listed in the table 2 along with the present work. The grown crystals are shown in the figure 3.7a.

12. Effect of temperature gradient on the growth of crystals during chemical vapour transportation

During the crystal growth, the position of the ampoule in the temperature profile and the profile itself are very important [28]. No work has been reported about the effect of variation of temperature gradient inside the furnace during the crystal growth. The radial temperature distribution profiles arranged in the two zone horizontal furnace have typical guassian shape. The minimization of the convection air current through the two zones can be achieved by using ceramic wool at the two openings along with the plugs. The thermal decoupling of the two zones can be effectively done by producing a separation of 3 cms between the heating coils. This separation imparts a 'dip' in the temperature profiles (fig. 3.4) and, by this we can arrange a temperature gradient between Ts (Hot zone temperature) and Td (Cold zone temperature) for each profile.
Figure 3.8 Cyclic process of the chemical transport in a closed system.
Table 2. Growth Parameters

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Hot zone °C</th>
<th>Cold Zone °C</th>
<th>Growth Time (hrs)</th>
<th>Size mm²</th>
<th>Ampoule Length (mm)</th>
<th>Ampoule Diameter (mm)</th>
<th>Transporting Agent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS₂e₂</td>
<td>850</td>
<td>750</td>
<td>504</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>Br₂</td>
<td>21</td>
</tr>
<tr>
<td>WS₂e₂</td>
<td>1055</td>
<td>890</td>
<td>504</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>I₂</td>
<td>21</td>
</tr>
<tr>
<td>WS₂e₃</td>
<td>800</td>
<td>700</td>
<td>96</td>
<td>---</td>
<td>190</td>
<td>22.5</td>
<td>Br₂</td>
<td>22</td>
</tr>
<tr>
<td>WS₂e₃</td>
<td>800</td>
<td>870</td>
<td>192</td>
<td>6</td>
<td>250</td>
<td>13</td>
<td>Br₂</td>
<td>30</td>
</tr>
<tr>
<td>WS₂e₄</td>
<td>800</td>
<td>780</td>
<td>144</td>
<td>4-6</td>
<td>250</td>
<td>13</td>
<td>I₂</td>
<td>30</td>
</tr>
<tr>
<td>WS₂e₅</td>
<td>1000</td>
<td>980</td>
<td>&gt; 60</td>
<td>120</td>
<td>250</td>
<td>13</td>
<td>SeCl₄</td>
<td>30</td>
</tr>
<tr>
<td>WS₂e₆</td>
<td>1000</td>
<td>850</td>
<td>120</td>
<td>4-15</td>
<td>250</td>
<td>13</td>
<td>SeCl₄</td>
<td>30</td>
</tr>
<tr>
<td>Wₓ₂e₂ Nbₓ Seₓ₂</td>
<td>975</td>
<td>950</td>
<td>144</td>
<td>60</td>
<td>250</td>
<td>9-13</td>
<td>SeCl₄</td>
<td>31</td>
</tr>
<tr>
<td>Wₓ₂e₂ Nbₓ Seₓ₂</td>
<td>900</td>
<td>810</td>
<td>120</td>
<td>7</td>
<td>200</td>
<td>24</td>
<td>I₂</td>
<td>Present work</td>
</tr>
<tr>
<td>Wₓ₂e₂ Nbₓ Seₓ₂</td>
<td>900</td>
<td>830</td>
<td>120</td>
<td>6.2</td>
<td>200</td>
<td>14</td>
<td>DVT</td>
<td>do</td>
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<tr>
<td>Wₓ₂e₂ Nbₓ Seₓ₂</td>
<td>900</td>
<td>830</td>
<td>120</td>
<td>5</td>
<td>200</td>
<td>24</td>
<td>DVT</td>
<td>do</td>
</tr>
</tbody>
</table>

Prepared by Beehive Digital Concepts Cochin for Mahatma Gandhi University Kottayam
It is assumed that these kinds of ‘dips’ enhance the transportation of the vapour species efficiently and, was observed that at a temperature gradient of $\Delta T = 70 \, ^\circ\text{C}$ the maximum size of the crystals were obtained for a constant period of time [29]. Temperatures arranged in different stationary temperature profiles (STP’s) are listed in the table 3.

Table 3. STP’s Data

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Hot zone ($^\circ\text{C}$)</th>
<th>Cold zone ($^\circ\text{C}$)</th>
<th>Temperature Gradient $\Delta T$ ($^\circ\text{C}$)</th>
<th>Time days</th>
<th>Size mm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>629</td>
<td>603</td>
<td>50</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>808</td>
<td>750</td>
<td>60</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>900</td>
<td>830</td>
<td>70</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>970</td>
<td>890</td>
<td>80</td>
<td>5</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

13. Conclusion

Tungsten diselenide crystals can be grown at lower concentration of iodine in lesser time by virtue of selecting the growth parameters from the theoretical calculations. Same conditions are also used for the growth of titanium doped WSe$_2$ crystals. The influence of temperature gradient on the growth of WSe$_2$ crystals are thoroughly studied. The particular temperature profile which is very close to the theoretical limits are produced inside the furnace and WSe$_2$ crystals of 7 mm$^2$ had grown.
References

17. H. Shanker, J.I. Lauritzer (Jr), R.J. Corruccini and S.T. Loberger, NBS