Chapter 2

Growth of MoSe$_{2-x}$Te$_x$ ($x = 0.25, 0.5, 1, 1.5, 1.75$)

Single crystals

Man has admired crystals ever since he realized the beauty and rarity of crystals. The subject crystal growth forms a frontier area of research in science and technology. Owing to their vivid physical and chemical properties the availability of appropriate crystalline material is a crucial factor for the development of advanced technologies as well as for breakthrough in applied and basic sciences. Crystals are the prime candidates for the fabrication of optoelectronic devices, high efficiency solar cells, fiber optic communication, wear-resistive coating and so many other technological applications.

Crystal finds extensive applications in today’s advanced technology. Modern technology is based largely on materials such as semiconductors, ferrites, magnetic garnets, solid state lasers, piezo-electric, ultraviolet and infrared sensitive crystals and crystalline films for micro-electronic and computer industries. All these involve research in crystal growth and characterization. This chapter is due to the chemical vapor transport technique (CVT) for the growth of molybdenum dichalcogenides crystals. It also includes some discussion about the growth mechanism of these crystals, which is based on the surface features of grown crystals.
2.1 HISTORICAL BACKGROUND OF CRYSTAL GROWTH

Crystal growth has been for a long time one of the fascinating observations where the atomic nature of matter clearly shows itself. Since the first attempts to study crystal growth, it has been realized that the subject involves the study of equilibrium between crystal and surrounding medium as well as the study of kinetics of growth. Fundamental aspects of crystal growth had been derived from early crystallization experiments in the 18th and the 19th century. Theoretical understanding started with the development of thermodynamics in the late 19th century [1] with the development of nucleation and crystal growth theories and the increasing understanding of the role of transport phenomena in the 20th century. The phenomena of under cooling and supersaturating and the heat of crystallization were already recognized in the 18th century by Fahrenheit and by Lowitz [2].

The rates of nucleation and crystallization in glasses were the foundation to nucleation theories. The crystal surface with steps and kinks inspired Stranski [3] to define the work of separation of crystal units as repeatable steps as the basis of the first crystal-growth theories. With the understanding of facet formation as a function of the entropy of fusion, the role of screw dislocations as continuous step sources in the formation of growth hillocks was explained by Jackson [4]. With the generalized crystal growth theory of Burton, Cabrera and Frank [5-8], many growth phenomena could be explained. In the growth of crystals from a fluid medium (melt, solution or gas phase) the heat and mass transport phenomena also play a significant role, as was observed by Scheel [9]. The diffusion boundary layer defined by Noyes and Whitney [10] was used in the growth-rate equation of Nernst [11] and confirmed by interferometric measurements of concentration profiles around growing crystals by Berg [12]. Forced convection was recognized to be beneficial for diffusion-limited growth by Wulff [13] for open systems with stirrers, whereas smooth stirring in sealed containers can be achieved with the Accelerated Crucible
Rotation Technique ACRT [14,15]. The growth of inclusion-free crystals from the melt can be accomplished by observing the principles of “diffusional undercooling” [16,17] and “constitutional supercooling” [18]. There have been remarkable developments with respect to size and perfection of crystals, with silicon, sapphire, alkali and earth alkali halides reaching diameters up to 0.5 m. These advances in Czochralski, Kyropoulos, heat-exchanger method, and Bridgman–Stockbarger growth were accompanied by numerical simulations which have become increasingly powerful to predict the optimized conditions. Thus the period 1900-1940 saw enormous advances in the subject which studied in its own right and as a source of materials for scientific studies. In 1904, Nernst [11] applied boundary layer theory to solution growth and many of the ideas about growth of perfect crystals were formulated by Volmer [19], Kossel [20] and Stranski [21]. Most of the crystal growth techniques being used today were also developed in this period. The flame fusion method was described by Verneuil [22,23]. Spezia laid the foundation of hydrothermal growth [24-26]. Methods for growth from solid were developed by Sauver [27] and Pintsch [28]. Crystal pulling was studied by Czochralski as a method for investigating the rate of growth of metal crystals [29]. Bridgman and Stober [30, 31] described melt growth in crucibles and Stockbarger [32] improved this method. The preparation of single crystals from the vapor phase has been described by Wildervanck, Schafer and Nitsche [33-36], while Al-Hilli and Evans [37] devised a method of direct vapor transport without using halogen. However, further advances in computer modeling and in the reliability of the used physico-chemical data are required in order to increase the efficiency and precision of computer simulations and to allow the prediction of the best crystal-growth technology including growth parameters for the growth of new large and relatively perfect crystals.
2.2 DIFFERENT TECHNIQUES FOR CRYSTAL GROWTH

There are different techniques for crystal growth which are listed below:

1. Vapor Growth : Growth from vapor phase
2. Solution Growth : Growth from an aqueous solution
3. Melt Growth : Growth from a supercritical or fluid phase
4. Solid Growth : Growth from one or more solid phases

These techniques are adequately described in various text books and reviews [38-47]. Figure 2.1 displays the classification of different crystal growth techniques.

2.3 VAPOUR TRANSPORT TECHNIQUE

This is a widely applicable technique for growing high quality single crystals of compound materials. Several compounds which are not accessible by usual crystal growing methods such as modified Czochralski or Bridgman - Stockbarger techniques can be prepared by this method. It is particularly suited for high melting compounds or for those which decompose without melting. Vapor transport method is mostly preferred for the growth of layered single crystals as well as for the fabrication of thin layers of metals, insulators and semiconductor type materials. It is convenient for large scale operations i.e. from the coating of turbine blades to grow epitaxial layers of semiconductor materials. Leith [48] has given an excellent review of various methods for the growth of layered compounds. Aruchamy and Agarwal [49] have also discussed the materials aspect of layered semiconductors where, crystal growth of layered materials is observed. The present investigation is advancement in the field of crystal growth of layered materials. Work represented here aims to describe the growth of single crystals like 2H-MoSe$_{2-x}$Te$_x$ by Chemical Vapor Transport Technique using iodine as a transporting agent. Vapor transport technique is classified into following two classes:

1. Chemical Vapor Transport (CVT) technique
2. Sublimation or Direct Vapor Transport (DVT) technique
Figure 2.1: Classification of different crystal growth techniques.
2.3.1 Chemical vapor transport (CVT) technique

This technique involves the growth of single crystals in reactive gas atmosphere (generally halogens) and it mainly relies on a chemical reaction between the source material to be crystallized and the reactive gas (transporting agent). The reaction product is volatile and can be transported in the vapor phase at temperature well below the melting point of the compound. Transportation occurs between two zones having different temperatures. Usually the starting reaction occurs at a higher temperature and is reversed at the low temperature to set down molecules of the compound at the most favorable crystalline sites. Initially random deposition occurs until seed crystals are formed. After that preferential growth starts taking place on these seeds, resulting in the formation of large single crystals. The transportation of the reaction products in the vapor phase can be obtained by a continuous gas flow from external supplies or by its recirculation within a closed tubular ampoule, and depending on the method applied it is termed as open-tube reactor system or closed-tube reactor system respectively.

Open-tube system is in wide spread use for commercial thin film crystal growth [50-52]. In this type of system, the reactants are introduced in the gas stream, carried into the reactor region and decomposed at location of crystal growth.

In a closed tube reactor system, source material to be converted to crystal form along with transporting agent is sealed in a tube which may be either evacuated or filled with inert gas. The tube is subjected to temperature gradient to promote reactions and transport of the crystal material from the source to crystallization region. The nature of chemical reaction will determine the temperature direction of transport [51]. For exothermic reaction, transport is toward region of higher temperature, while endothermic reaction will provide transport toward lower temperature for crystal growth. Schafer [51] mentioned some examples of both the types of reactions. The cyclic process
taking place in closed-tube reactor type chemical vapor transport technique is depicted in figure 2.2.

Figure 2.2 Illustration of the cyclic process of chemical vapor transport in a closed system.

In principle, one can transport unlimited amount of starting material with a small amount of transporting agent. The rate of transport of the compound (M) in gm/sec is given by Nitsche [56] as

\[
M = LdP(T', T'', dG, C_1)
\]  

(2.1)

where \( T' \) and \( T'' \) are the temperatures at hot end and cold end respectively,
d\( P \) is the difference between partial pressures of the reaction product at temperatures \( T' \) and \( T'' \),
C_t is concentration of the transporting agent,
L is conductance of the system, which is a function of the ampoule geometry and the physical processes involved in the vapor transport, and
dG is the change in Gibb’s free energy in the reaction.

Different parameters mentioned in the transport equation (2.1) have the following significance.

(dG): It has been found by Schafer [51] that an optimum transport occurs when reaction is not far from equilibrium, i.e. dP is maximum for values of dG closed to zero. For chalcogenides, the halogens are most commonly used as transporting agents, since their dG values are quite low.

(C_t): Nitsche [56] found a value of 5 mg/cc for C_t to be a good starting point for experiment.

(L): The conductance of the system depends on the mode of transport of the reaction product. This is controlled principally by the total vapor pressure inside the ampoule, most of which is due to the volatile transporting agent.

There are three possible mechanisms.

(a) At low pressure and with small ampoule diameter diffusion is the only important transport mechanism.
(b) As the pressure or the diameter is increased, convection current set up by the thermal gradient rapidly becomes more important.
(c) In the initial reaction equation,
    compound + transporting agent = reaction product.

Usually there are equal numbers of molecules in the vapor phase on each side. If this is not so, there will be a pressure gradient along the ampoule and a laminar flow of the reaction product will take place.

(\(T_1\), \(T_2\)) dP: depends strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature.
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$T^\prime$: the crystallization temperature should be within the stability range of the required crystal type.

$(T' - T^\prime)$: The temperature difference is altered to control $dP$, and so to vary the vapor transport rate. However, this cannot be increased indefinitely without causing polycrystallization [53] as explained below:

Molecules condensing on to a flat surface from the vapor loose potential energy, i.e. they acquire binding energy, $E'$. However, their thermal energy gives them a probability, $p'$ of evaporation as

$$p' \propto e^{\frac{E_v}{k_B T}}$$

where, $E_v$ is the chemical potential, $k_B$ is the Boltzmann Constant and $T$ is the temperature.

The rate of condensation, $n$ (mole·sec$^{-1}$·cm$^{-2}$) is controlled by the partial pressure of the vapor $P$ (atm.) and average molecular velocity $v$ (cm/sec).

$$n = L_o P v$$

where $L_o$ is the Loschmidt’s constant = $2.687 \times 10^{19}$/ (cm$^3$.atm.).

There will be a pressure, $P^\prime$, where the rate of condensation and evaporation are equal. In reality, when a molecule condenses on a crystal, it will tend to migrate over the surface before evaporation. If whilst migrating, it finds a site of greater binding energy, $E^\prime\prime$ such as a kink or step on the crystal surface, the probability of evaporation drops. Equilibrium in such cases will occur at pressure $P^\prime\prime$.

If the partial pressure has a value between $P'$ and $P^\prime\prime$, molecules will only condense on the site of greater binding energy $E^\prime\prime$. Under this condition crystals that have already formed will grow but no new crystals will form unless impurities bind some molecules more firmly to the ampoule wall to form a seed crystal.

Since the net number of molecules condensing is limited by the number of growth sites, the rate of transport must not be too high.
Otherwise the partial pressure of the reaction product will exceed \( P' \) and polycrystallization will occur.

Finally, Nitsche [56] arrived at the following general rules for the successful growth of crystals by vapor transport technique:

- The rate of transport must not exceed the rate of growth of the seeds.
- The optimum crystallization temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.
- The crystallization chamber should be large in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.
- The temperature distribution in the crystallization chamber should be as uniform as possible to avoid partial re-evaporation of already grown crystals.
- Well developed crystals can be formed more easily in large diameter tubes, where transporter convection determines the rate of transport.
- The temperature difference between the reaction and the growth chamber can be made smaller when wider tubes are used, since the gas flow here is the rate determining parameter.

**2.3.2 Direct vapor transport (DVT) technique**

The CVT is very useful technique for the growth of large sized layered single crystals. But the main hitch with this technique is usually the grown crystals are found incorporated with an active impurity in the form of a small amount of the transporting agent during the growth process. This affects the thermal, optical and electrical properties of the grown crystals at a considerable extent. In some cases, for example \( \text{ZrSe}_2 \) grown using transporting agent \( \text{I}_2 \), the transporting agent remains strongly adsorbed on the surface or incorporated between the layers and becomes difficult to remove it completely [54].
Several researchers used the direct vapor transport or sublimation method (without transporting agent) in order to avoid the contamination due to transporting agent [48, 49, 54-58]. Their work shows that it is possible to grow fairly large crystals of TMDCs and their solid solutions without transporting agent.

2.4 CRYSTAL GROWTH OF MOLYBDENUM DICHALCOGENIDES

Material aspect of molybdenum dichalcogenides (as discussed in chapter 1) from both research as well as technological point of view led the optimization in growth conditions for these materials in a form (single crystal, polycrystalline powder, thin film etc.) suitable for a particular application. Several researchers reported crystal growth of Molybdenum dichalcogenides by vapor transport technique as summarized in table 2.1.

**Table 2.1** Growth parameters of MoX$_2$ (x = Se and Te) single crystals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (K)</th>
<th>Transporting agent</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H-MoSe$_{2-x}$Te$_x$</td>
<td>1093</td>
<td>Br$_2$</td>
<td>[42]</td>
</tr>
<tr>
<td>(x = 0 and 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2H-MoSe$_{2-x}$Te$_x$</td>
<td>1073</td>
<td>I$_2$</td>
<td>[46]</td>
</tr>
<tr>
<td>(x = 0 and 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2H-MoSe$_{2-x}$Te$_x$</td>
<td>1053</td>
<td>I$_2$</td>
<td>[50]</td>
</tr>
<tr>
<td>(0 ≤ x ≤ 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2H-MoSe$_2$</td>
<td>1033</td>
<td>TeCl$_4$</td>
<td>[52]</td>
</tr>
<tr>
<td>2H-MoTe$_2$</td>
<td>1173</td>
<td>Br$_2$</td>
<td>[54]</td>
</tr>
</tbody>
</table>

However, the single crystals of almost all layered compounds can be grown by both chemical as well as direct vapor transport technique; researchers generally prefer the chemical vapor transport technique due to following reasons.

- Use of transporting agent enhances the vapor transport rate which increases the growth and results in the formation of larger sized single crystals compared to those grown by direct vapor transport technique.
In the case of CVT, nucleation takes place at a temperature well below that in the case of DVT. Keeping these parameters in mind, in the present work preference is given to the thorough use of chemical vapor transport technique to grow single crystals of MoSe$_{2-x}$Te$_x$ ($x = 0.25, 0.5, 1, 1.5, 1.75$).

### 2.4.1 Growth furnace

Dual zone horizontal furnace is the most important instrument for the work related to crystal growth while working with vapor transport. In the present research work, for growing the crystals we have used two-zone horizontal furnace. This type of furnace is capable to provide appropriate temperature gradient (for transport process to take place) over the entire ampoule. The temperature gradient within the furnace is maintained over a length of about 25 cm. Stability of the temperature plays an important role, therefore, for this purpose digital electronic temperature controllers were used.

The furnace was constructed by our University Science and Instrumentation Center (USIC) using a special sillimanite threaded tube (grade KR 80 GA HG) open at both the ends, 50 cm in length, 7 cm outer diameter, 5.6 cm inner diameter with threaded pitch of 3 mm. Super Kanthal A1 wire of 17 SWG was wound directly on the threaded tube into two different zones or regions. The tube was enclosed in glass wool and then in the insulating brick slabs constructed locally and the brick slabs were fully enclosed in thick asbestos sheets, and the entire assembly was supported in a steel frame work. This arrangement is shown in figure 2.3a. The power supplied to the furnace windings was regulated by the control circuit shown in figure 2.3b. The two regions of windings were provided with independent power supplies and temperature controllers. Transformers with 70, 80 and 100 V taps with 20 A current capacities in secondary windings were used to supply sufficient power in order to achieve the required high temperature.
Figure 2.3a Dual zone horizontal furnace with co-axially loaded ampoule (a) Threaded sillimanite tube, (b) glass wool, (c) insulating bricks, (d) asbestos sheet, (e) steel jacket, (f) two different zones, (g) ampoule.

Figure 2.3b Control circuit diagram of the crystal growth furnace.

2.4.2 Ampoule

High quality quartz tubes of various diameters, having a melting point of about 1500 °C were used for growth experiments. Tubes having internal diameter 22 mm, outer diameter 25 cm and length 250 mm were found to be more suitable for the growth of 2H-MoSe$_2$$_x$Te$_x$ materials. One end of the ampoule was sealed and the other end was drawn into a neck and joined to another (8 mm inner and 10 mm outer diameter) quartz tube to connect it to the vacuum system for evacuation after introducing the source material. Cleaning of ampoule is an important step in the crystal growth process. The ampoule was first washed with boiled water along with a suitable alkali solution,
after that it was washed with a hot mixture of concentrated HNO₃ and HF (49 %) taken in equal proportion. Then the washing was followed by double distilled water. Again it was washed with a mixture of concentrated HNO₃ and H₂SO₄ taken in equal volume. Ampoule was filled with 20 ml HF and heated at 343 K temperature for about half an hour in order to make the inner surface of ampoule slightly rough which is useful for the better growth of crystals. Finally washing was done by double distilled water for 8 to 10 times. Then the clean ampoule was transferred into the constant temperature oven kept at 373 K and left overnight to make it moisture free.

2.4.3 Crystal growth by vapor transport technique

A complete process of crystal growth of transition metal chalcogenides can be divided in two parts as compound synthesis and crystal growth. For synthesizing molybdenum dichalcogenides, required materials in the elemental form were taken in a stoichiometric proportion and filled in a quartz ampoule duly cleaned and dried by the process explained above. A total amount of constituent materials used was 10 gm in each experiment. Table 2.2 summarizes the purity and make of source elements. The ampoule is then evacuated at 10⁻⁵ torr and sealed. The sealed ampoule was shaken thoroughly for proper mixing of the constituent materials. In the sealed ampoule, the constituent element in the powder form was then distributed uniformly all over the length and kept in the horizontal furnace co-axially in the centre. The temperature was slowly increased up to 1123 K at a rate of 60 K/hour. The slow heating was necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements. Comparatively larger size of the ampoule and the uniform distribution of the powder minimize the chances of explosion. The ampoule was kept at this constant temperature for 75 hours. After this period, the furnace was slowly cooled down to room temperature at a rate of 30 K/hour and then switched off. The process results in a freely flowing, shiny, homogenous polycrystalline powder (charge) of related compound.
Table 2.2 Purity of source elements used and their source of supply.

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity (%)</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum (Mo)</td>
<td>99.990</td>
<td>Alfa Aesar, A Johnson Mathey Company</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>99.999</td>
<td>Alfa Aesar, A Johnson Mathey Company</td>
</tr>
<tr>
<td>Tellurium (Te)</td>
<td>99.999</td>
<td>Alfa Aesar, A Johnson Mathey Company</td>
</tr>
<tr>
<td>Iodine (I)</td>
<td>99.990</td>
<td>Alfa Aesar, A Johnson Mathey Company</td>
</tr>
</tbody>
</table>

The charge prepared in the above manner was well mixed by vigorous shaking of the ampoule. For actual growth process, the material was transferred into another thoroughly cleaned quartz ampoule along with iodine. Iodine of the quantity 1 mg/cc of the ampoule volume was sealed in the thin capillary and placed in a quartz ampoule. This ampoule with charge of material and capillaries was again evacuated at 10\(^{-5}\) torr and then sealed. The ampoule was then inserted into a dual-zone horizontal furnace. The growth of single crystals of any compound depends upon various different parameters such as

- Length of the ampoule
- Purity of the source materials used
- Quality of the quartz tube
- Achievement of proper vacuum
- Amount and type of transporting agent
- Temperature distribution of the furnace
- Appropriate proportion of constituent element
- Time duration for crystal growth
- Rate of increase and decrease of temperature

The growth parameters for 2H-MoSe\(_2\)\(_x\)Te\(_x\) (x = 0.25, 0.5, 1, 1.5, 1.75) single crystals are shown in Table 2.3. In all the cases as stated earlier, iodine was used as a transporting agent. The rate of increment
and decrement of temperature in all the cases was 60 K/hour. In all cases the growth temperatures were maintained for 120 hours. This complete process results in single crystals of related material. Figure 2.4 shows the photographs of as grown crystals of 2H-MoSe$_{2-x}$Te$_x$.

**Table 2.3** Growth parameters of 2H-MoSe$_{2-x}$Te$_x$ single crystals.

<table>
<thead>
<tr>
<th>Growth parameters</th>
<th>2H-MoSe$_{2-x}$Te$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x = 0.25$</td>
</tr>
<tr>
<td>Source zone temperature (K)</td>
<td>1143</td>
</tr>
<tr>
<td>Growth zone temperature (K)</td>
<td>1093</td>
</tr>
<tr>
<td>Ampoule dimensions (length in cm X diameter in cm)</td>
<td>22 x 2.5</td>
</tr>
<tr>
<td>Vacuum level (torr)</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Name and amount of transporting agent</td>
<td>Iodine 1 mg/cc</td>
</tr>
<tr>
<td>Growth period (hour)</td>
<td>120</td>
</tr>
<tr>
<td>Rate of increment of temperature (K/hour)</td>
<td>60</td>
</tr>
<tr>
<td>Rate of decrement of temperature (K/hour)</td>
<td>60</td>
</tr>
<tr>
<td>Crystal dimensions (mm X mm X mm)</td>
<td>13 x 9 x 0.5</td>
</tr>
<tr>
<td>Physical appearance</td>
<td>Shiny Silver</td>
</tr>
</tbody>
</table>
2.5 STUDY OF CRYSTAL GROWTH MECHANISM

The beauty and sparkle of many faceted crystals found all over the earth’s crust have attracted tremendous interest in them since the beginning of recorded history. During most of this history, crystals have been treasured primarily because of their ornamental value.

\textbf{Figure 2.4} Grown single crystals of \textbf{a.} 2H-MoSe$_{1.75}$Te$_{0.25}$, \textbf{b.} 2H-MoSe$_{1.5}$Te$_{0.5}$, \textbf{c.} 2H-MoSeTe, \textbf{d.} 2H-MoSe$_{0.5}$Te$_{1.5}$, \textbf{e.} 2H-MoSe$_{0.25}$Te$_{1.25}$.
More recently single crystals of different materials are being used in many new applications such as solid state devices. Because many properties of solids can be best studied with single crystals, the increasing interest in nature of solids requires the crystals grown under controlled conditions. Till the date almost all of naturally occurring crystals have been synthesized in laboratories. During the course of such synthesis, a great deal has been learned about the crystal growth process itself.

2.5.1 Crystal growth theories
As soon as stable nuclei are formed in a supersaturated or supercooled system, they begin to grow into crystals of visible size. Many proposed mechanisms of crystal growth may broadly be discussed under a few general headings.

The surface energy theories are based on the postulation that the shape of a growing crystal is that which has a minimum surface energy. The diffusion theories presume that matter is deposited continuously on a crystal face at a rate proportional to the difference in concentration between the point of deposition and the bulk of the solution. Suggestion by Volmer [64], that the crystal growth is a discontinuous process, taking place by adsorption, layer by layer, on the crystal surface led to the adsorption-layer theories. Some critical reviews made by various authors provide a comprehensive account of the historical development of many crystal growth theories [65-69, 75].

(a) Surface energy theory
An isolated droplet of a fluid is most stable when its surface free energy, and thus its area, is a minimum. Gibbs [70] suggested that the growth of a crystal could be considered as a special case of this principle: the total free energy of a crystal in equilibrium with its surroundings at constant temperature and pressure would be a minimum for a given volume. Therefore, if a crystal is allowed to grow in a supersaturated medium, it should develop into an 'equilibrium'
shape, i.e. the development of the various faces should be in such a manner which ensures that the whole crystal has a minimum total surface free energy for a given volume.

Of course, a liquid droplet is very different from a crystalline particle; in the former the constituent atoms or molecules are randomly dispersed, whereas in the latter they are regularly located in a lattice structure. Gibbs was fully aware of the limitations of his simple analogy, but Curie [47] found it as a useful starting point for an attempt to evolve a general theory of crystal growth and in 1901 Wulff [48] showed that the equilibrium shape of a crystal is related to the free energies of the faces; he suggested that the crystal faces would grow at rates proportional to their respective surface energies.

![Diagram](image)

**Figure 2.5a** (Velocities of crystal growth faces) invariant growth; **b.** overlapping growth.

The surface energy and the rate of growth of a face, however, should be inversely proportional to the reticular or lattice density of the respective lattice plane, so that faces having low reticular densities would grow rapidly and eventually disappear. In other words, high index faces grow faster than low one. The velocity of growth of a
crystal face is measured by the outward rate of movement in a direction perpendicular to that face. In fact to maintain constant interfacial angles in the crystal, the successive displacements of a face during growth must be parallel to each other. Except for the special case of a geometrically regular crystal, the velocity of growth will vary from face to face. Figure 2.5a shows the ideal case of a crystal that maintains its geometric pattern as it grows. Such a crystal is called 'invariant'. The three equal A faces grow at an equal rate; the smaller B faces grow faster; while the smallest face C grows fastest of all. In practice, a crystal does not always maintain geometric similarity during growth; the smaller, faster-growing faces are often eliminated, and this mode of crystal growth is known as 'overlapping'. Figure 2.5 (b) shows the various stages of growth of such a crystal. The smaller B faces, which grow much faster than A faces, gradually disappear from the pattern.

So far there is no general acceptance of the surface energy theories of crystal growth and there is also little quantitative evidence to support them. These theories, however, still continue to attract attention, but their main defect is their failure to explain the well-known effects of supersaturation and solution movement on the crystal growth rate.

(b) Adsorption layer theory
The concept of a crystal growth mechanism based on the existence of an adsorbed layer of solute atoms or molecules on a crystal face was first suggested by Volmer in 1939 [64]. Volmer's theory, or as some prefer to call it, the Gibbs-Volmer theory, is based on thermodynamic reasoning. When units of the crystallizing substance arrive at the crystal face they are not immediately integrated into the lattice, but merely lose one degree of freedom and are free to migrate over the crystal face (surface diffusion). There will, therefore, be a loosely adsorbed layer of integrating units at the interface, and a dynamic equilibrium is established between this layer and the bulk solution. Atoms, ions or molecules will link into the lattice in positions where
the attractive forces are greatest, i.e. at the 'active centres', and under ideal conditions this step-wise build-up will continue until the whole plane face is completed (figure 2.6a and b). Before the crystal face can continue to grow, i.e. before a further layer can commence, a 'centre of crystallization' must come into existence on the plane surface, and in the Gibbs-Volmer theory it is suggested that a monolayer island nucleus, usually called a two-dimensional nucleus, is created (figure 2.6c).

![Figure 2.6a](image)

**Figure 2.6a** (Mode of crystal growth without dislocations) migration towards desired location; **b.** completed layer; **c.** surface nucleation.
Figure 2.7 Kossel’s model of growing crystal surface containing flat surfaces A, steps B, kinks C, surface adsorbed growth units D, edge vacancy E and surface vacancy F.

Kossel [71] in 1934 gave a model of a growing crystal face which is depicted in figure 2.7. It envisages that an apparently flat crystal surface is in fact made up of moving layers (steps) of mono-atomic height, which may contain one or more kinks. In addition, there will be loosely adsorbed growth units (atoms, molecules or ions) on the crystal surface and vacancies in the surfaces and steps. Growth units are most easily incorporated into the crystal at a kink; the kink moves along the step and the face is eventually completed. A fresh step could be created by surface nucleation, and this frequently commences at the corners.

Figure 2.8 Development of growth spiral starting from a screw dislocation.

A crystal should grow fastest when its faces are entirely covered with kinks. It is well known, for example, that broken crystal surfaces
rapidly 'heal' and then proceed to grow at a much slower rate. However, many crystal faces readily grow at quite faster rates at relatively low supersaturation, far below those needed to induce surface nucleation. Crystals of iodine, for example, can be grown from the vapor at 1 per cent supersaturation and at a rate about 10-1000 times greater than those predicted by classical theory [72]. So it must be concluded that the Kossel [71] model, and its dependence on surface nucleation, is unreasonable for growth at moderate to low supersaturation.

A solution to the dilemma came when Frank [4] postulated that few crystals ever grow in the ideal layer-by-layer fashion without some imperfection occurring in the pattern. Most crystals contain dislocations, which cause steps to be formed on the faces and promote growth. Of these, the screw dislocation is considered to be important for crystal growth, since it obviates the necessity for surface nucleation. Once a screw dislocation has been formed, the crystal face can grow perpetually 'up a spiral staircase'. Figure 2.8a-c indicates the successive stages in the development of a growth spiral starting from a screw dislocation. The curvature of the spiral cannot exceed a certain maximum value, determined by the critical radius for a two-dimensional nucleus under the conditions of supersaturation in the medium in which the crystal is growing.

2.5.2 Surface morphology

Surface micro-topographic studies provide an easy and powerful mean to understand the actual process of crystal growth. In the present work observation of microstructures on crystal surfaces was accomplished with the help of a metallurgical microscope. This microscope shown in figure 2.9 has been designed by ‘Carl Zeiss’ for rapid examination of grind, polished and as-grown surfaces of the objects and hence it affords every convenience called for this kind of examination. Being an incident light type microscope, the objective has an infinite intersectional distance, i.e. the specimen lies in the
front focal plane of the objective and its image is formed at infinity. The microscope contains a permanently built-in table lens, which together with the eyepiece forms a telescope. A 25 V, 100 W filament lamp (Tungsten-Halogen lamp) serves as a source of illumination. The operation and function controls of this microscope are elegantly shown in the schematic diagram shown in figure 2.10. The sample for microtopographic analysis is placed on glass slide. The glass slide is mounted on the mechanical stage with the specimen holder (14). The instrument is switched on with the help of on/off switch (12). Using the Reflected-light illumination control (11), the lamp voltage is set appropriately using the lamp voltage display (10). From eyepiece (1) and objective lens (17), the surface structure of the sample is viewed. The specimen holder can be moved front-back and left right using the co-axial stage drive (15) to bring the desired area in field of view. With the help of co-axial coarse and fine drive (13), the specimen holder can be moved up and down and the surface can be very accurately focused. The optical microscope is finally attached to the CCD camera with a resolution of 0.5X (X being 1000 times). The whole picture of the surface microstructure can be viewed live on the computer screen and stored in the memory. Finally, a print out of the well-focused surface microstructure of the specimen is taken out using the attached computer system.
Figure 2.9 Optical microscope (make: Carl Zeiss, Model: Axiotech 100).
Figure 2.10 Schematic diagram of Axiotech 100

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<td>3</td>
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Figure 2.11a-h Surface micro-topographs of 2H-MoSe$_{1.75}$Te$_{0.25}$ single crystals.

Figures 2.11a-h show the surface microtopographs of the 2H-MoSe$_{1.75}$Te$_{0.25}$ single crystals. The following surface features are
observed: (1) Triangular and spiral growth layers covered the whole surface, (2) A few growth centres i.e. triangular hillocks, and triangular growth layers emanate from these centres. Misorientation of the crystal to the imposed light leads to the development of the large number of lines all over the surface; they appear to radiate from the misoriented crystal, and cut across the straight triangular growth steps, causing no visible deformation of their triangular morphology. The most striking feature observed along the irregular lines is the occurrence of the small triangular growth spirals. These triangular and composite spirals, emanating from points on the lines, have only few turns (see figure 2.11h). It is to be expected that the triangular spirals will form at screw dislocations.

Surface microtopographs shown below indicate how considerable information can be secured in qualitative manner without even measurement.

![Figure 2.12a Trigon with Plane Slope. b. Trigon with concave curvature.](image)

It is seen that trigons are two types, those which are relatively fairly deep and those which are very shallow. There is a curious statistic in that the dimensions within the two types, both in extension and in depth, do not cover a very great range. In figure 2.12a the trigon descends to a pyramidal point and in the figure 2.12b the trigon has a flat base.
The nearly equidistant fringe spacing within the sides of the figure 2.12a trigon indicate the plane slope, whereas the differential spacing in the figure 2.12b trigon indicates the existence of the concave curvature.

![Figure 2.13a](image)

**Figure 2.13a** Shallower trigon within the shallow trigon. **b.** Trigons sited on line dislocation.

Figure 2.13a indicates the shallower trigons within the shallow trigons. Although the shallow trigons have strictly outline, crossed fringes reveal in a striking way one special characteristic often found, namely an asymmetry in the surrounding surface. This is shown in figure 2.13b. Here is a crossed fringe system in which trigons appear to sit on line discontinuities. This is not uncommon and it is almost certainly a line dislocation on which the trigons fixed. The crossed fringes near the large main trigon show clearly the growth mechanism. The growth sheets have progressed from below and halted at the dislocation. They sweep round and the incompletion leaves the trigon but the sweep round leads to a slowing down in the growth rate [41].
Figure 2.14a-h  Surface micro-topographs of 2H-MoSe$_{1.5}$Te$_{0.5}$ single crystals.
In the cases of 2H-MoSe<sub>1.75</sub>Te<sub>0.25</sub> (figures 2.11f), 2H-MoSe<sub>1.5</sub>Te<sub>0.5</sub> (figures 2.14a-d), 2H-MoSe<sub>0.5</sub>Te<sub>1.5</sub> (figures 2.15a-d) and 2H-MoSe<sub>0.25</sub>Te<sub>1.75</sub> (figures 2.16a-d), growth spirals are observed on these crystals surface indicating that their growth was driven by screw dislocation mechanism. In growth from vapor, theory [63] predicts that the growth of a crystal surface with steps will be the result of

**Figure 2.15a-f** Surface micro-topographs of 2H-MoSe<sub>0.5</sub>Te<sub>1.5</sub> single crystals.
three processes: (1) Transport of molecule from vapor to surface of solid (2) Diffusion of adsorbed molecule to steps.

Figure 2.16a-f Surface micro-topographs of 2H-MoSe$_{0.25}$Te$_{1.75}$ single crystals.

(3) Diffusion of molecules along the edge of a step to a kink. The rate of advancement of a straight step is given as [41]

$$ V = 2(\sigma - 1)X_s ne^{-\omega' / k_BT} $$

(2.3)

where $(\sigma - 1)$ is the supersaturation,

$X_s$ is the mean distance that a molecule will wander over the surface of a crystal between the time it hits and time it evaporate,
\( \nu \) is a frequency factor and is of the order of frequency of atomic vibration,
\( \omega \) is the evaporation energy and
\( k_B \) is the Boltzmann constant.

When the mean distance between kinks \( (X_0) \) is very small compared to \( X_s \) that means \( (X_s >> X_0) \), than the molecule will have a high probability of adhering to steps if adsorbed near it regardless of orientation of the steps. This will result in the rate of advancement of step independent of the crystal orientation and finally the formation of circular spirals on the surface of the growing crystals. On the other hand if the rate of advancement of a step is dependent on the crystallographic orientation than the shape of growth spirals will be polygonal. Here in both the cases growth spirals exhibit hexagonal shape, which confirms that the growth speed of both materials were dependent on crystallographic orientation [73-75].

Figure 2.14g shows the inclusion acting on the flat surface of the 2H-MoSe\(_{1.5}\)Te\(_{0.5}\) crystals. Inclusion is generated due to the strong non equilibrium conditions of growth and lack of temperature gradient uniformity. Grain boundaries in CVT grown 2H-MoSe\(_{1.5}\)Te\(_{0.5}\) usually appear between grains of different polytypes. Grain presents massive defects and their occurrence can lead to crack. Another feature is observed on the surface of 2H-MoSe\(_{1.5}\)Te\(_{0.5}\) (figure 2.14f) which shows that the crystal surface of 2H-MoSe\(_{1.5}\)Te\(_{0.5}\) is growing by the lateral spreading of the layers [76].

Figure 2.15e-f shows the planars, are known as hexagonal prism shaped empty spaces with typical size up to several hundred micrometers in with and lengthier thickness. Some planars are open it means they exposed to crystal surface. In addition to this, faint line observed on the surface of the 2H-MoSe\(_{1.5}\)Te\(_{0.5}\) single crystal (see figure 2.14b) that runs through the centre of the spiral which is geometrically related to the spiral, considered to have been formed after the spiral.
Hexagonally shaped pits are formed on the surface of the $2H$-$MoSe_{0.5}Te_{1.5}$ shown in figure 2.15d. As far as the hexagonal pits retain the pyramidal shape, continuous disturbance occur in the growth direction and will produce screw dislocations. Here, it is believed that this hexagonal shaped pit pattern is very close to the growth mechanism during the crystal growth.

A crystal generally contains a number of dislocations. The fact that for the supercoolings some crystals failed to grow while other grew at varying rates provides a basis for the supposition that $2H$-$MoSe_{2-x}Te_x$ crystals in our studies had different degrees of perfection. The crystals which failed to grow at slight supercoolings were evidently more perfect, while those growing at considerable rates under the same conditions contained faults, presumably of a dislocation character. This is confirmed by direct observations of individual crystals, among which some have smooth face (figures 2.15e-f) and some have spirals (figures 2.11, 2.14, 2.15, 2.16). We may also suppose that in the process of growth, the growth of the structure of face undergoes certain changes leading to the change in the growth rate. At some extent, the hexagonal spiral shown in figure 2.16a shows the straight edges correspond to a sharp minimum in the growth rate as a function of crystallographic orientation [77].

### 2.6 IMPORTANT CONCLUSIONS

Some conclusions may be drawn on the basis of observations made during the work carried out as presented in this chapter are listed below.

1. High quality large sized single crystals of $2H$-$MoSe_{2-x}Te_x$ ($x = 0.25, 0.5, 1, 1.5, 1.75$) can be grown using chemical vapor transport technique where iodine is transporting agent.

2. Crystals of all these compounds are found to grow in the form of platelets having micrometer sized thickness.
3. Trial and error method is used to optimize the growth temperatures and to get the large size crystals for all the compounds.

4. Crystals of $2H-MoSe_{1.75}Te_{0.25}$, $2H-MoSe_{1.5}Te_{0.5}$, $2H-MoSe_{0.5}Te_{1.5}$ and $2H-MoSe_{0.25}Te_{1.75}$ were found to be grown by screw dislocation mechanism. The microtopography studies of $2H-MoSeTe$ prove that surface of $2H-MoSeTe$ grow by plane sheets and that the incompletion of the sheets leaves the trigons.

Thus single crystals of $2H-MoSe_{2-x}Te_x$ were grown successfully but still there are number of parameters which are untouched and need further investigations to be made.

- All the compounds were grown by chemical vapor transport technique by using only iodine as a transporting agent. Several materials are known today which can be used as a transporting agent. Therefore the growth of these materials by different transporting agents may provide the information about a best suitable transporting agent. Author had also tried to grow same compounds by direct vapor transport method but in this case they were found to be growing in the form of needle shape.

- $MoSe_2$ and $MoTe_2$ compounds are known to exist in seven different crystal structures but no such work is reported for intermediate compounds. We have accomplished this in the present task.

- In the present work we have optimized the growth temperatures by keeping a constant temperature gradient between source zone and growth zone. The reaction period was also kept constant. Effect of varying these parameters on the growth of these crystals is not known.

After this successful synthesis of $2H-MoSe_{2-x}Te_x$ single crystals, it is necessary to carry out the stoichiometry conformation and structural characterizations of the grown materials. The next chapter provides stoichiometry conformation as well as the structural characterizations.
through the studies of energy dispersive analysis of x-rays, powder x-ray diffraction and electron diffraction for the grown materials. This chapter also includes the TGA studies.
REFERENCES

8. N. Cabrera, Verlag Chemie, **56**, (1952), 294.