Chapter 2

2.1 BASIC INFORMATION OF CRYSTAL GROWTH

The developments in the field of solid-state physics are mainly due to the availability of good quality single crystals. The growth of single crystals has been developed over the years to meet the needs for basic research and applications. As the demand for crystals with specific property increases day-by-day, new techniques have been evolved to meet the requirements of the end user.

Three major stages are involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices.

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 attempt 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] and 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 undercooling, supersaturating and the heat of crystallization were already recognized in the 18th century by Fahrenheit and 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 Rouelle and Frankenheim [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 super cooling” [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 and weights of nearly 500 kg. 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 was 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 [24-26] laid the foundation of
hydrothermal growth. Methods for growth from solid were developed by Sauver [27] and Pintsch [28]. Crystal pulling was studied by Czochralski [29] as a method for investigating the rate of growth of metal crystals. Bridgman and Stockbarger [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 METHODS FOR CRYSTAL GROWTH

Different methods for crystal growth are:

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].

2.3 VAPOR TRANSPORT TECHNIQUE

The growth of single crystal material from the vapor phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapor phase by sublimation, condensation and sputtering of elemental materials. To obtain single crystals of high melting point materials, this method is used which 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 presented in this chapter aims to describe the growth of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) single crystals by chemical vapor transport technique using iodine as a transporting agent. These compounds are grown in the form of single crystals for the first time in the family of transition metal dichalcogenides.

Vapor transport technique is classified into following two classes:

1) Chemical Vapor Transport (CVT) technique
2) Sublimation or Direct Vapor Transport (DVT) technique

### 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 takes 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. 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.

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 [53] as

$$M = LdP(T', T'', dG, C_r)$$  \hspace{1cm} (2.1)

Where, $T'$ and $T''$ are the temperatures at hot end and cold end respectively,

$dP$ is the difference between partial pressures of the reaction product at temperatures $T'$ and $T''$, 

\hspace{1cm}
$C_t$ 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,

$dG$ 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 [53] 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.
$(T', T'') \, dP$ depends strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature.

$T''$: The crystallization temperature should be within the stability range of the required crystal type.

$(T' - T'')$: 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 [54] 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

$$p' \propto e^{\left(\frac{E'}{k_B T}\right)}$$  \hspace{1cm} (2.2)

Where, $E_w$ is chemical potential, $k_B$ is Boltzmann constant and $T$ is 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).

$$n = L_o P v$$  \hspace{1cm} (2.3)

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

There will be a pressure $(P')$, 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 $E''$ such as a kink or step on the crystal surface, the probability of evaporation drops. Equilibrium in such cases will occur at pressure $P''$.  

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Priyanka F. Desai/Ph.D. Thesis/Department of Physics/S. P. University/March 2014
If the partial pressure has a value between $P'$ and $P''$, molecules will only condense on the site of greater binding energy $E''$. 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 [53] arrived at the following rules for the successful growth of crystals by vapor transport technique:

1. The rate of transport must not exceed the rate of growth of the seeds.

2. The optimum crystallization temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.

3. The crystallization chamber should be large in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.

4. The temperature distribution in the crystallization chamber should be as uniform as possible to avoid partial re-evaporation of already grown crystals.

5. Well developed crystals can be formed more easily in large diameter tubes, where transporter convection determines the rate of transport.

6. The temperature difference between the reaction and the growth chamber can be made smaller when wider tubes are used, since the gas flow is the rate determining parameter.
2.3.2 Direct Vapor Transport (DVT) Technique

The vapor transport is very useful technique for the growth of large sized layered single crystals. But the main hitch with this technique is that the grown crystals are found with the incorporation of 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 ZrSe$_2$ grown using I$_2$, the transport agent remains strongly adsorbed on the surface or incorporated between the layers and becomes difficult to remove it completely [55].

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].

2.4 CRYSTAL GROWTH OF Cr$_x$Mo$_{1-x}$Se$_2$ (x=0.25, 0.50, 0.75)

Material aspect of Cr$_x$Mo$_{1-x}$Se$_2$ (x=0.25, 0.50, 0.75) (as discussed in chapter 1) from both the research as well as technological point led the optimization in growth conditions for these materials in a form (single crystal, polycrystalline powder, thin film etc.) suitable for a particular application.

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 we have made a thorough use of chemical vapor transport technique to grow single crystals of Cr$_x$Mo$_{1-x}$Se$_2$ (x=0.25, 0.50, 0.75).
2.4.1 Growth Furnace

Furnace is the most important component for the work related to crystal growth. In the present research work, for growing the crystals we used dual zone horizontal furnace. This type of furnace is able 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 250 mm. Stability of the temperature plays an important role, therefore, for this purpose electronic temperature controllers were used.

![Photograph of dual zone horizontal furnace](image)

**Figure 2.1** Photograph of dual zone horizontal furnace

The furnace was made by AGNI GmbH, Aachen, Germany as shown in Figure 2.1 using gas tight alumina (99.97% Al₂O₃) tube open at both the ends, 1100 mm in length, 70 mm outer diameter, 60 mm
inner diameter with 1750°C heating capacity. Heated length of tube was 600 mm and it was divided into two zones of 250 mm each with 40 mm gap between zones. Furnace is casing in double walled construction with forced air cooling between walls. Thus outer cell is not hot even at higher temperature. Furnace insulation was completely of ceramic fibres with low thermal capacity. Kanthal super heating elements were installed on both the sides of the tube to radiate freely. Two zone regulation unit was installed under the furnace. B type PtRh thermocouples were used for regulation of each zone. FY-800 microprocessor based digital PID controllers were used.

2.4.2 Ampoule

High quality quartz tubes of various diameters, having a melting point of about 1773K were used for growth experiments. Tubes having internal diameter 22 mm, outer diameter 25 mm and length 250 mm were found to be more suitable. 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 343K 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 373K and left overnight to make it moisture free.
2.4.3 Crystal Growth by Chemical Vapor Transport Technique

A complete process of crystal growth of transition metal dichalcogenides can be divided in two parts as compound synthesis and crystal growth. For synthesizing, 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 2.1 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.

**Table 2.1** 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>Chromium (Cr)</td>
<td>99.99</td>
<td>Sigma-Aldrich, USA</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>99.99</td>
<td>Sigma-Aldrich, USA</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>99.99</td>
<td>Sigma-Aldrich, USA</td>
</tr>
<tr>
<td>Iodine (I)</td>
<td>99.99</td>
<td>Alfa Aesar, A Johnson Mathey Company</td>
</tr>
</tbody>
</table>

The temperature was slowly increased up to 1273K at a rate of 60K/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 100 hours. After this period, the furnace was slowly cooled down to room temperature at a rate of 60K/hour and then switched off. The process results in a freely flowing, shiny, homogenous polycrystalline powder (charge) of related compound.

The charge (compound) 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 2 mg/cm$^3$ of the ampoule volume was sealed in the thin capillary and placed in a quartz ampoule. This ampoule with charge of material and capillary 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 increment and decrement of temperature

The growth parameters for Cr$_x$Mo$_{1-x}$Se$_2$ ($x=0.25$, 0.50, 0.75) single crystals are shown in Table 2.2. In all the cases iodine (2 mg/cm$^3$) was used as a transporting agent. The rate of increment and decrement of temperature in all the cases was 60K/hour. This complete process results in thin opaque platelets and shiny gray single crystals of related material. Figure 2.2 shows the photographs of as grown crystals of Cr$_x$Mo$_{1-x}$Se$_2$ ($x=0.25$, 0.50, 0.75).

![Figure 2.2](image_url)

**Figure 2.2** Grown single crystals of (a) Cr$_{0.25}$Mo$_{0.75}$Se$_2$ (b) Cr$_{0.5}$Mo$_{0.5}$Se$_2$ (c) Cr$_{0.75}$Mo$_{0.25}$Se$_2$
Table 2.2 Growth parameters of Cr$_x$Mo$_{1-x}$Se$_2$ (x=0.25, 0.50, 0.75) single crystals

<table>
<thead>
<tr>
<th>Compound Preparations</th>
<th>Temperature Distribution</th>
<th>Growth Time (hours)</th>
<th>Dimensions (of the largest crystal) (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (K)</td>
<td>Time (hours)</td>
<td>Cold Zone (K)</td>
</tr>
<tr>
<td>Cr$<em>{0.25}$Mo$</em>{0.75}$Se$_2$</td>
<td>1273</td>
<td>100</td>
<td>1173</td>
</tr>
<tr>
<td>Cr$<em>{0.5}$Mo$</em>{0.5}$Se$_2$</td>
<td>1273</td>
<td>95</td>
<td>1193</td>
</tr>
<tr>
<td>Cr$<em>{0.75}$Mo$</em>{0.25}$Se$_2$</td>
<td>1273</td>
<td>90</td>
<td>1223</td>
</tr>
</tbody>
</table>

2.5 KINETICS OF CRYSTAL GROWTH

The purpose of this part is to understand the basic ideas of crystal growth from the vapor, only referring to the experimental evidence when it is relevant to our point of view. This section classifies the condition of growth from vapor and classification is based on the kind of surface (weather singular or diffuse) where the growth promoting source is located.

2.5.1 Classification of Growth Conditions

1. The growing surfaces are nonsingular (diffuse) and as such do not require a source of steps. We called this as a dendritic growth.

   From the experimental point of view dendritic growth appears to be favoured by the following conditions

   a) A volume diffusion field operates which favors nonsingular surfaces.

   b) High super saturation and high equilibrium concentration producing a high rate of growth in such a way that the growing surface does not wait for the condensing atoms to diffuse to it but goes forward to catch them.
2. The growing surfaces is singular (vicinal) and require source of steps. We called this layer growth.

In layer growth to simultaneous and to some extent, independent possesses are going on as

a) Creation of steps at a source – less regular polyhedron growth
b) Motion of steps away from the source – a whisker growth

The type of growth occurring on a given crystal surface might depend on the rate. A layer type occurring at low rates of growth might become dendritic at sufficiently high rates when the driving force for the growth is very large.

2.5.2 Crystal Surface Mechanism

The mechanism of crystal growth is unambiguously determined by the structure of the crystal face as depicted in Figure 2.3.

Figure 2.3 Growing crystal surfaces showing face, step and kink
### 2.5.2.1 Classification of Crystal Surface Sites

<table>
<thead>
<tr>
<th>Position of atom</th>
<th>No. of saturated bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within Face (1)</td>
<td>5</td>
</tr>
<tr>
<td>Within Step (2)</td>
<td>4</td>
</tr>
<tr>
<td>Within Kink (3)</td>
<td>3</td>
</tr>
<tr>
<td>Upon Step (4)</td>
<td>2</td>
</tr>
<tr>
<td>Upon face (5)</td>
<td>1</td>
</tr>
</tbody>
</table>

The detachment of these atoms will lead to a change in surface energy of the crystal for all but the atom at the kink position. At this position, the atom has 3 saturated bonds, and 3 unsaturated bonds. In all crystals, the kink site has the following properties:

- It determines the equilibrium of an infinitely large crystal with the ambient phase.
- Its chemical potential is equal to the chemical potential of the crystal.
- Its desorption energy of the kink site is equal to the crystal enthalpy of evaporation.
- If a system is supersaturated, it will be favourable for an adatom arriving at the kink site to be incorporated into the crystal.

### 2.5.2.2 Classification of Crystal Faces

The equilibrium shape of crystals is bounded by the crystal faces with the lowest specific surface energies. A crystal face at a small angle to one of these low energy faces, however, will not be atomically flat; but will consist of terraces and steps. In fact, crystal faces can be divided into three groups as shown in Figure 2.4.

1. F (flat) faces. These are parallel to at least two dense atomic rows.
2. S (stepped) faces. These are parallel to one dense atomic row.
3. K (kinked) faces. These are not parallel to any dense atomic rows.

![Growing crystal surfaces showing face, step and kink](image)

Figure 2.4 Growing crystal surfaces showing face, step and kink

F faces are generally atomically flat. However, as temperature is increased and entropic factors become more important, F faces undergo a surface roughening transition at a critical temperature known as the roughening temperature, $T_r$. The atomically rough crystal faces (i.e. S, K and F faces at temperatures above $T_r$) grow by a different mechanism to the atomically flat faces (F faces at temperatures below $T_r$).

**2.5.2.3 Crystal Growth Mechanisms**

a) Continual growth mechanism for atomically rough faces

If S face, K face or F face at a temperature above $T_r$, it is atomically rough and can grow continuously. Growth rate is fast and is simply proportional to the flux of atoms from the parent phase, i.e. the growth is diffusion controlled. The rate of crystal growth ($R$) is given by:

$$ R = \lambda \Delta \mu $$

(2.4)

Where, $\lambda$ is the kinetic coefficient and $\Delta \mu$ is the super saturation.
Hence the growth rate depends linearly upon the super saturation. The kinetic coefficient is proportional to the surface roughness (in terms of the probability of finding a kink site), and to the exponent of the activation energy, for incorporation of a building unit into the lattice. Typical values of $R$ are $10^{-4} - 10^{-1}$ (cm-sec$^{-1}$). Crystals that grow by the continual growth mechanism tend to have rounded morphologies. Atomically flat F faces (i.e. F faces at temperatures below $T_r$), however, cannot grow by this mechanism.

b) Layer growth of flat faces

1. Consider an atomically flat crystal face belonging to perfect defect less crystal. A single adatom on such a face is bound more weakly than an adatom in a cluster of adatoms on the surface. Consequently, there is an energy barrier to the formation of each new crystal layer. This situation is the 2D analogue of homogeneous nucleation, and hence the rate of growth of this face will be determined by the frequency of the formation of 2D critical nuclei.

2. If the F crystal face is not perfect, and in particular if screw dislocations are present, then these screw dislocations represent a non-vanishing source of steps which alleviate the necessity of a 2D nucleation growth mechanism. Instead the rate of crystal growth is determined by the rate of the lateral movement of the steps (Figure 2.5).

![Figure 2.5](image)  
**Figure 2.5** Development of growth spiral starting from screw dislocation
2.6 SURFACE MICROTOPOGRAPHY

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 2.6 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 2.7. 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. 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 2.6 Optical microscope (make: Carl Zeiss, Model: Axiotech 100)
Figure 2.7 Schematic diagram of Axiotech 100

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<table>
<thead>
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<tbody>
<tr>
<td>1</td>
<td>Eyepieces</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Binocular Phototube 20°</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Pushrod (to change beam path)</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Luminous-field diaphragm slider</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>Compartment for 3D illuminator shutter</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>Pushrod for reflected Light aperture diaphragm</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>Centering screw for reflected-light aperture</td>
<td>14</td>
</tr>
<tr>
<td>15</td>
<td>Coaxial stage drive</td>
<td>16</td>
</tr>
<tr>
<td>17</td>
<td>Objective nose piece</td>
<td>18</td>
</tr>
<tr>
<td>19</td>
<td>Trans. light luminous-field diaphragm</td>
<td>20</td>
</tr>
<tr>
<td>21</td>
<td>Compartment for DIC slider</td>
<td></td>
</tr>
</tbody>
</table>
Typical surface features visible on the as grown Cr$_x$Mo$_{1-x}$Se$_2$ ($x=0.25, 0.50, 0.75$) single crystals shown in Figure 2.8 were frequently observed. Study of microstructures reveals a large number of crystallographically oriented spirals on the grown faces of these crystals, which suggests a screw dislocation mechanism involved in the growth of these crystals [59]. In general, presence of screw dislocations in grown crystals shows the characteristic property of the growth from gaseous phase. The pattern of growth spirals, both with unique or with multiple burger vectors strongly depends on the rate of movement of dislocations and atomic steps in different crystallographic directions relative to the faces. Further, the feature of polygonized spirals reflects the symmetry of that face of the crystal and the formation develops perpendicular to the direction of crystal growth. Thus the peculiarities of the growth of faces are directly reflected with the distinctive features of the growth conditions. Figure
2.8(a-c) of Cr<sub>x</sub>Mo<sub>1-x</sub>Se<sub>2</sub> (x=0.25, 0.50, 0.75) single crystals depict the initiation and the advancement of hexagonal growth spirals originating from a point and gives a clear view of the left handed (Clockwise) growth spirals on the surface[60,61]. Figure 2.8(d) shows the large nondislocation hillocks appear on a surface of Cr<sub>0.25</sub>Mo<sub>0.75</sub>Se<sub>2</sub> single crystal. It appears when the crystal grows at high temperature and its interfacial energy is small. Nature of growth layers of the hillocks is typical of bunched layers and the large nondislocation hillocks composed of thick growth steps. It is difficult to resolve elementary steps by conventional optical microscopy; it is possible that in some cases the hillocks have originated at emergence points of screw dislocations but the spiral layers at their origins have not been revealed due to the poor optical resolution of microscope. It is also possible that the dislocations emitting the steps have moved out of the plane of observations [62]. Figure 2.8(e) represents another example of nondislocation hillocks observed on the face of Cr<sub>0.5</sub>Mo<sub>0.5</sub>Se<sub>2</sub> single crystal. The sides of these hillocks are not polygonized and illustrate a spiral elevation. In vapor growth an increase in growth temperature leads to a rounding off of spirals. These hillocks are present may be due to iodide impurity [62]. Figure 2.8(f) is clearly showing presence of Frank-Read dislocation on the face of Cr<sub>0.75</sub>Mo<sub>0.25</sub>Se<sub>2</sub> single crystal. This dislocation emerges due to multiplication in slip plane under the shear stress during the growth [62].

2.7 CONCLUSIONS

Some conclusions may be drawn on the basis of observations made during the work carried out as discussed in this chapter which are as under.

1. For the synthesis of shiny, fine, and free flowing charge of Cr<sub>x</sub>Mo<sub>1-x</sub>Se<sub>2</sub> (x=0.25, 0.50, 0.75), the temperature of the ampoule was maintained at 1273K.
2. High quality large sized single crystals of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) can be grown by chemical vapor transport technique using iodine as a transporting agent.

3. Crystals of all these compounds are found to grow in the form of platelets having micrometer sized thickness.

4. Growth temperatures of all compounds were optimized for largest crystal size by trial and error method.

5. Crystals of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) were found to be grown by screw dislocation mechanism.

6. On the surface of \( \text{Cr}_{0.25}\text{Mo}_{0.75}\text{Se}_2 \) and \( \text{Cr}_{0.5}\text{Mo}_{0.5}\text{Se}_2 \) crystals nondislocation hillocks are appeared and in the case of \( \text{Cr}_{0.75}\text{Mo}_{0.25}\text{Se}_2 \) Frank-Read dislocations are prominent.

Thus single crystals of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) were grown successfully first time so there are number of aspects untouched and needs investigations to be made. After the growth and microtopographic study of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) crystals, we have determined the structure of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) by powder X-ray diffraction. We have also carried out the electron diffraction study of \( \text{Cr}_x\text{Mo}_{1-x}\text{Se}_2 \) (\( x=0.25, 0.50, 0.75 \)) crystals which is discussed in the following chapter.
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Chapter 2