

CHAPTER : 3

GROWTH OF CRYSTALS BY VAPOUR TRANSPORT TECHNIQUE

3.1 INTRODUCTION :

The growth of crystals depends on their melting point, vapour pressure and the magnitude of solubility in water. On the basis of this view point, different methods of crystal growth are:

1. Growth from melt
2. Growth from vapour phase
3. Growth from aqueous solution

The techniques are described in various text books and reviews [1 - 8]. The majority of compounds of the transition metal dichalcogenides belonging to MX_2 group is insoluble in water and decompose before their melting points are reached. Therefore, the growth of such crystals from the melt and aqueous solution is not possible. Hence, the growth of single crystals of these compounds from vapour phase technique was found to be most suitable.

3.2 GROWTH FROM VAPOUR TRANSPORT METHODS

Vapour transport methods are generally preferred due to their relative simplicity and wide applicability. Chemical vapour transport (CVT) and sublimation (or direct vapour transport) methods are distinguished.

3.2.1 CHEMICAL VAPOUR TRANSPORT TECHNIQUE:

This is a widely applicable method. 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. Application of this technique stems from the work of

van-Arkel [9 - 11] on the growth of metal single crystals in halogen atmospheres. Its use for the growth of layer compounds is at the suggestion of Nitsche and his coworkers [12 - 14]. Most transition metal dichalcogenide layer compounds are prepared by this method [15-18]. Also, ternary compounds containing phosphorus such as Ni PS₃, Fe PS₃, Fe PSe₃ [19, 20], Mn P Se₃, Cd PSe₃ [21], Ga_{2/3} PS₃, Al_{2/3} P S₃ [22 - 23] and Pd PS, PdPSe [24 - 25] have been prepared by CVT.

CVT technique mainly relies on a chemical reaction between the source material to be crystallized and a transporting agent. The reaction product is volatile and can be transported into the vapour phase at temperature well below the melting point of the compound. Transport occurs between two zones having different temperatures. Usually the starting reaction occurs at a higher temperature and is reversed at the low temperature to deposit molecules of the compound at the most favourable crystalline sites. Initially random deposition occurs until seed crystals are formed. Thereafter growth preferentially occurs on these seeds, and large single crystals are formed. The transportation of the reaction products in the vapour phase can be obtained by a continuous gas flow from external supplies or by its recirculation within a closed tubular ampoule. The process is depicted in Fig. 3.1. In principle, the resultant is, one can transport unlimited amount of starting material with only a small amount of transporting agent. The rate of transport of the compound in gm/sec. is given by Nitsche et al. [13] as

$$m = L dp (T', T'', d, \alpha) \quad \dots\dots\dots 3.1$$

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'',

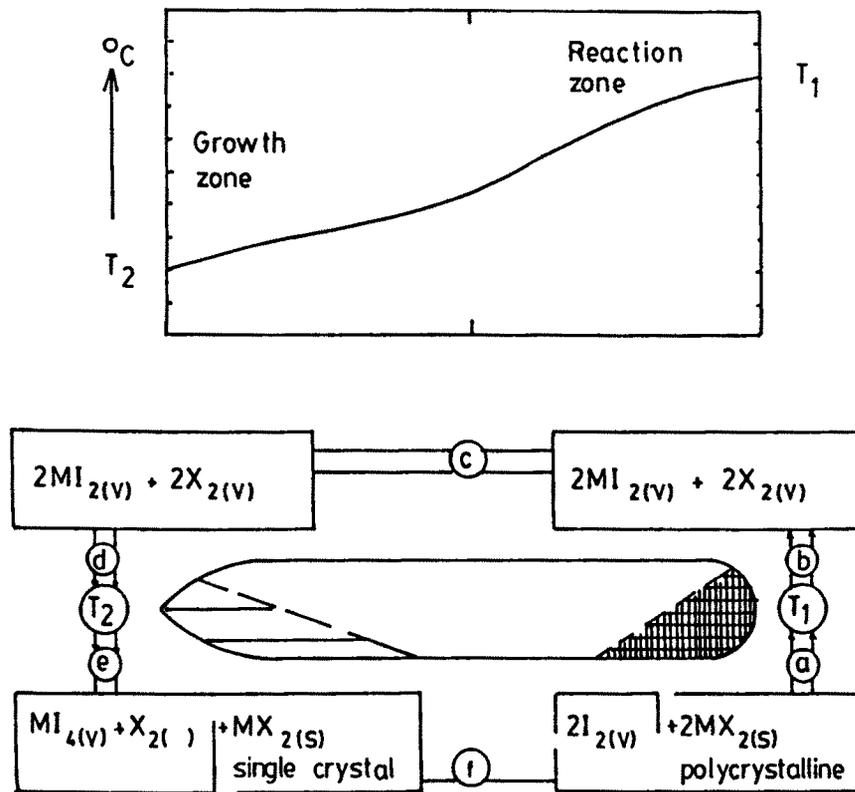


Fig. 3.1 Illustration of the cyclic process of chemical vapour transport in a closed system

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 vapour transport.

and dG is the change in Gibb's free energy in the reaction.

Different parameters mentioned in the transport equation (3.1) have the following significance.

(dG): It has been found by Schafer [26] that optimum transport occurs when the reaction is not far from equilibrium, i.e. dp is maximum for values of dG not far from zero. For chalcogenides, the halogens are most commonly used as transporting agents, since their dG values are quite low.

(c_t): Nitsche [12] 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 vapour 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,



There are usually equal numbers of molecules in the vapour 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 [27].

T'' : the crystallisation 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 vapour transport rate. However, this cannot be increased indefinitely without causing polycrystallisation, as explained below:

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

$$p' \propto \exp(E_v/kT)$$

The rate of condensation, n (mole/sec/cm²) is controlled by the partial pressure of the vapour P (atm) and average molecular velocity, V (cm/sec).

$$n = L_0 P V$$

where L_0 is the Loschmidt's constant = $2.687 \times 10^{19}/(\text{cm}^3 \text{ atom})$

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'' .

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 polycrystallisation will occur.

Finally, Nitsche [13] arrived at the following rules for the successful growth of crystals by vapour transport technique :

1. The rate of transport must not exceed the rate of growth of the seeds,
2. The optimum crystallisation temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.
3. The crystallisation chamber should be large in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.

4. The temperature distribution in the crystallisation 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 here is the rate determining parameter.

3.2.2 DIRECT VAPOUR TRANSPORT TECHNIQUE :

The layered crystals grown by the CVT method usually incorporate small amount of the transport agent, which may remain as an active impurity and affect the measured properties. 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 [28].

In order to avoid contamination by the transport agent Al Hilli and Evans [28] and Agarwal and coworkers [29] used the direct vapour transport or the sublimation method (without transport agent). Their work showed that it is possible to grow fairly large crystals of TMDCs and their solid solutions. Author has made a thorough use of this technique to grow mixed crystals of SnS_xSe_{2-x} in the present investigation. Details of the growth procedure will be discussed in the relevant chapters of the thesis.

3.3 EXPERIMENTAL SET UP :

3.3.1 DUAL ZONE HORIZONTAL FURNACE :

The furnace is the most important part of present research work to grow the crystals of TMDCs. Two zone furnace provides an appropriate temperature gradient over the entire ampoule. Normally the temperatures employed are fairly high. The temperature gradient within the furnace is required over a length of about 25 cm. Stability of the temperature plays an important role, therefore, for this purpose electronic temperature controllers were used.

The furnace was constructed in our University Science and Instrumentation Center (USIC) by using a special sillimanite threaded tube (grade KR 80 GA HG) closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm, imported from Koppers Fabriken Feuerfester, Germany. Super Kanthal A1 wire of 17 SWG was wound directly on the furnace tube into two different zones or regions. The tube was enclosed in the hot face insulating brick slabs constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and the entire assembly was supported in a steel framework. This arrangement is shown in Fig. 3.2. The power supplied to the furnace windings was regulated by the control circuit shown in Fig. 3.3. The two regions of windings were provided with independent power supplies and temperature controllers. Transformers with 70,80 and 100V taps with 20A current capacity in secondary windings were used to supply sufficient power in order to achieve the required high temperature.

Microprocessor based temperature programmers purchased from M/s. Indotherm Instruments Pvt. Ltd., Mumbai, were used to control the temperatures in the two zones of the furnace. The fluctuations in the local

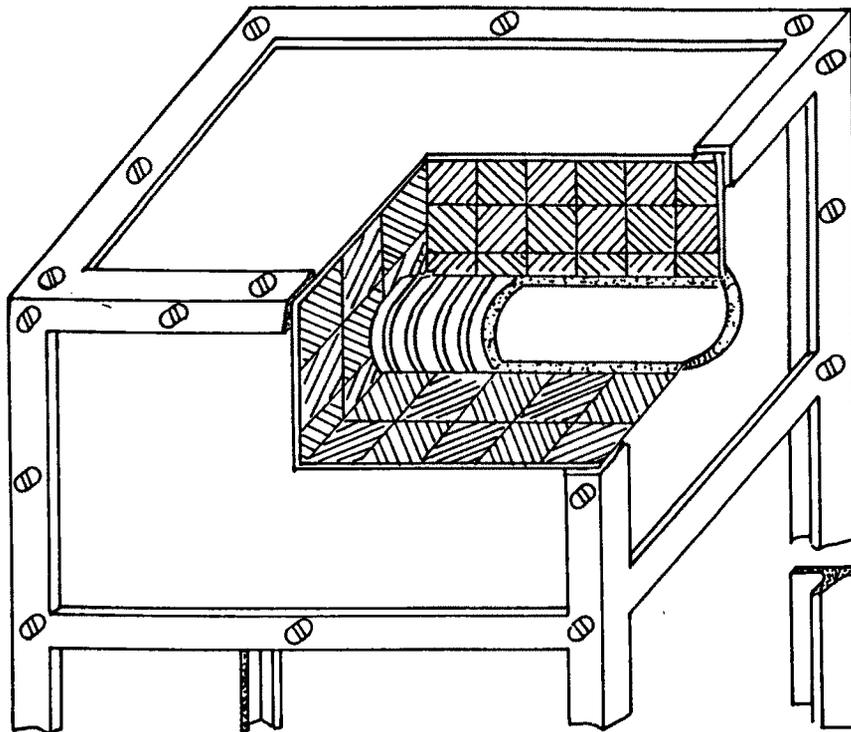


Fig. 3.2 Schematic representation of the furnace.

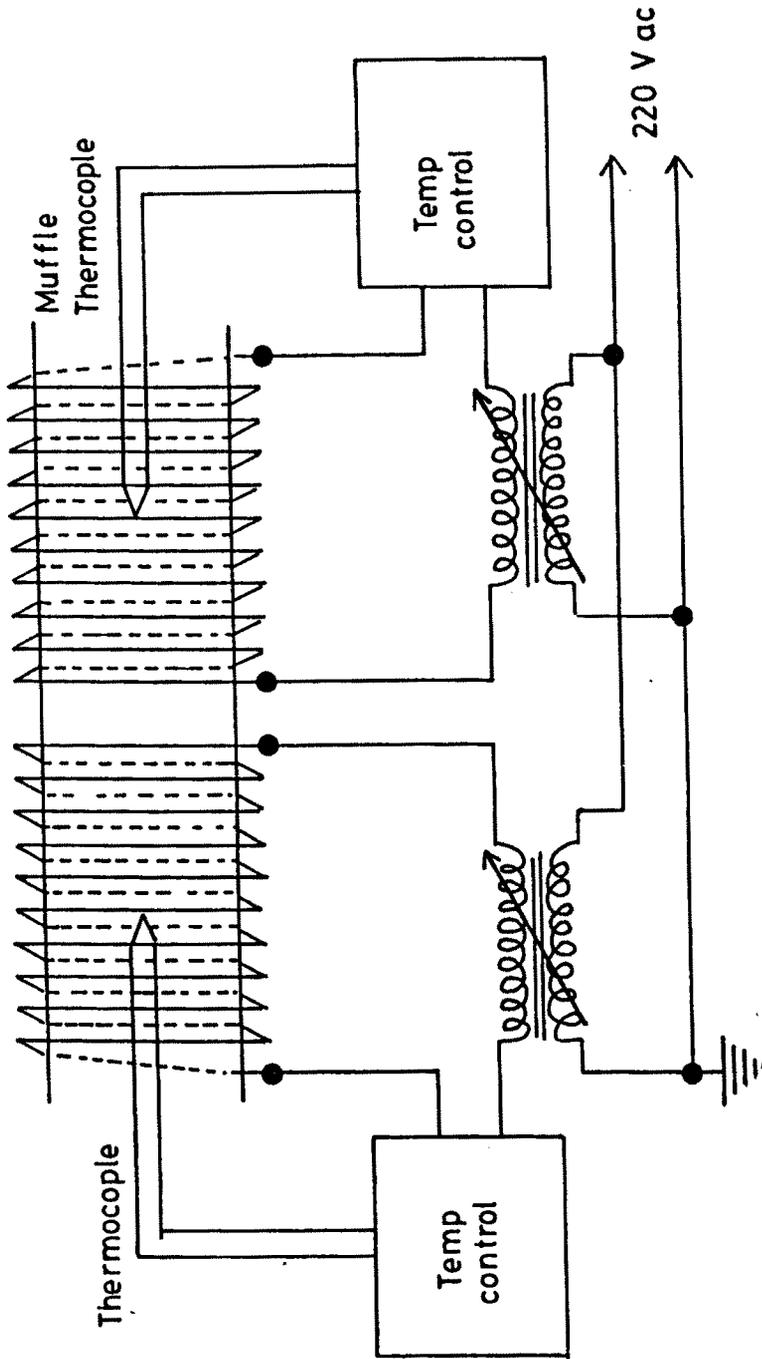


Fig 3.3 Control circuit for regulating the power.

electrical supply were controlled by AC voltage stabilizer with 180-260 V input and $230 \pm 1\%$ output volts of capacity 3 kVA. The output of stabilizer was fed to the primary windings of the transformer, which heated the furnace windings and helped to maintain the stability of growth conditions. With the help of temperature programmers, a required temperature gradient could be established across the length of the working tube in the required temperature range. Thermocouples used were Pt (13 %), Rh. Pt. and temperature programmers were calibrated for the above thermocouples. It was found that the thermocouples were stable over the prolonged use in the furnace, and they were supported within the furnace tube itself showing the furnace tube temperature.

3.3.2 AMPOULE :

High quality fused quartz tubes of various diameters, having a melting point of about 1500°C were used for growth experiments. Tubes having internal 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 10 mm inner diameter quartz tube to connect it to the vacuum system for evacuation after introducing the source materials.

3.4 CRYSTAL GROWTH :

3.4.1 CLEANING OF AMPOULE :

First the ampoule was washed with boiled water along with a suitable detergent, after that it was washed with a hot mixture of concentrated HNO_3 and HF (49 %) taken in equal quantity. Then the washing was followed by double distilled water. Again it was washed with a mixture of concentrated HNO_3 and H_2SO_4 taken in equal volume. Finally washing was

done by double distilled water for 8 to 10 times. Then the clean ampoule was transferred into SICO constant temperature oven at 100°C and left overnight to make it moisture free.

3.4.2 CHARGE PREPARATION :

For the charge preparation the required materials (Table 3.1) for growth were taken in a stoichiometric ratio and filled up in a transparent ampoule duly cleaned and dried by the process explained above. The ampoule containing the source material was then connected to a vacuum system and precaution was taken that the vacuum was brought so slowly that none of the materials from the ampoule could enter the vacuum system. A total charge of about 10 gm was used in each experiment. When the vacuum was being reached, the ampoule was tapped slowly so that any air between the particles of the materials was removed. When a vacuum of the order of 10^{-5} torr was reached, the ampoule was sealed off at the neck.

The sealed ampoule with the elemental powder was shaken thoroughly to ensure proper mixing of the contents. The mixture was then distributed uniformly all over the length of the ampoule. The ampoule was thus ready for keeping it in the furnace.

After keeping the ampoule at an appropriate place in the horizontal furnace, the temperature was slowly increased. The temperature and the period for which the ampoule was kept in the furnace depended upon the material, which was being grown. 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 well uniform distribution of the powder minimize the temperature rise to prevent an explosion. After specific time of heating at the required temperature, the furnace was switched off. After bringing it to room temperature it was

Table 3.1: Materials used and their source of supply

Material	Purity (%)	Source	Appearance
Tin (Sn) Shot	99.999	Aldrich Chemical Co USA	Silver Shot
Sulphur (S)	99.998		Yellow
Selenium (Se) Powder, -100 Mesh	99.999		Black Powder
Iodine (I ₂)	99.99	British Drug House Ltd.	Black
Amonium Chloride (NH ₄ Cl)	99.99		White

observed that the ampoule had a fine free flowing, shiny homogeneous polycrystalline material.

Just as the specific conditions of temperature and reaction time are different for charge preparation, in the same way actual growth procedure also varies from material to material. The growth procedure and conditions for $\text{SnS}_x\text{Se}_{2-x}$ single crystals are thoroughly described and discussed in the relevant chapters.