CHAPTER 2

GROWTH OF SINGLE CRYSTALS BY A VAPOUR PHASE METHOD

2.1   Introduction

There are several methods for growing single crystals, the techniques being fully described in the text books and reviews[1-11]. The compounds of transition metal dichalcogenides TX_2 group are insoluble in water and they decompose before their melting point is reached which naturally prevents their growth from aqueous solution and growth from melt. Therefore attempts have been made to grow these crystals from vapour phase.

This method can be classified in the following two categories.

(1)   Chemical vapour transport method

(2)   Direct vapour transport method

2.2   Vapour Growth Technique

2.2.1   Chemical vapour transport method

This method, for the preparation of single crystals has been reported and found as a reliable method for crystal growth of metal dichalcogenides[12-17]. New theoretical attempts of vapour transport of solids are given by Lever[18-19], Mandel[20-21] and Arizumi and

Nishipanaga[22]. Kaldis [23,24] has shown that it is possible to grow crystals upto several cm in size by chemical vapour transport under well controlled nucleation conditions at smaller supersaturations. Transport reactions have been studied systematically by Schafer[25] for the preparation of high purity refractory metals.

Chemical vapour transport technique mainly depends on a chemical reaction between the source material to be crystallized and a transporting agent. The reaction product is volatile and can be transported in the vapour phase at temperatures 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 lower temperature to deposit molecules of compound at the most favourable crystalline sites. Initially, random deposition occurs and seed crystals are formed. The transport of the reaction products in the vapour phase can be obtained by continuous gas flow from external supplies or by its recirculation within a tubular ampoule. This is illustrated in Fig. 2.1. As a result, in principle, one can transport unlimited amount of the starting material with only a small amount of transporting agent.

Fig. 2.1   Illustration of the cyclic process of
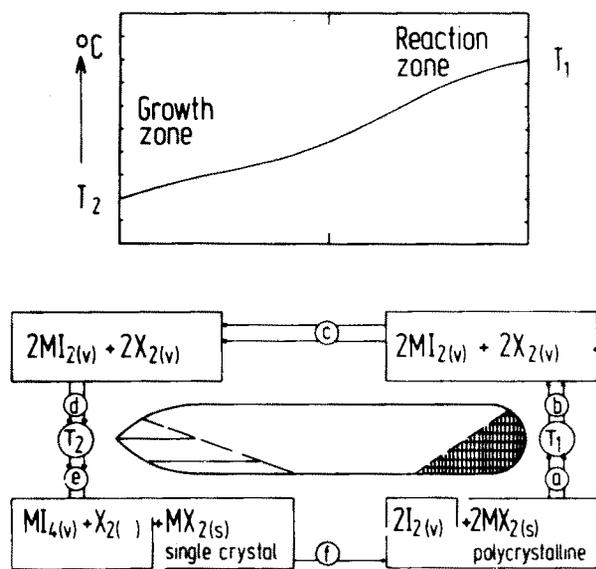   chemical transport in a closed system.

Fig. 2.1

The rate of transport of the compound in gm/sec. is given by Nitsche et al[13] as,

$$m = L.dp \ (T', T'', dG, C_t) \ . \hspace{2cm} (2.1)$$

where

T', T''   are the temperatures at hot and cold ends respectively

dp   difference between the partial pressures of the reaction product at temperature T' and T'',

dG   change in Gibb's free energy in the reaction,

C_t concentration of transporting agent,

L   conductance of the system, a function of the ampoule geometry and the physical processes involved in the vapour transport.

The above parameters in the transport equation (2.1) have the following significance.

(dG)   It has been found by Schafer[15] that optimum transport occurs when the reaction is not   far from the equilibrium, that is, dp is a maximum for values of dG near zero. For chalcogenides, the halogens are most commonly used as transporting

agents. Bromine gives better results for MoS_2 and $MoSe_2$[14].

(C_t)   Nitsche[16] 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 in the ampoule, most of which is due to the volatile transporting agent. Three different mechanisms are possible.

(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 currents set up by the thermal gradient rapidly become more important.

(c)   In the initial reaction equation,

Compound + Transporting Agent = Reaction product.

There are equal number 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[16]. Many
compounds, including MoS_2 have more than one
possible crystal structure, and their stability
is often temperature dependent. T", the crysta-
llization 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 polycrystallization,
as explained below.

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

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

The rate of condensation, n (molecules/sec . cm^2) is controlled by the partial pressure of the vapour, p (atmosphere) and the average molecular velocity, v (cm/sec.).

where $\quad n = L_o \, pv$

$\quad L_o =$ Loschmidts constant

$\quad\quad = 2.687 \times 10^{19}$ per (cm^3 atm).

There will be pressure, p', when the rates of condensation and evaporation are equal.

In reality, when a molecule condenses on to 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 step on the crystal surface, the probability of evaporation drops. Equilibrium will occur at lower pressure, p".

If the partial pressure has a value between p' and p", molecules will only condense on the sites of greater binding energy E". Under these conditions any 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 seed crystal.

Since the net number of condensing molecules

is limited by the number of growth sites, the rate of transport must not be too high. If the rate of transport is higher then the partial pressure of the reaction product will exceed p' and polycrystallization will occur.

Finally, Nitsche[13] gave the following rules for the successful growth by vapour 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 larger 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 form more easily in
        large diameter tubes, where transporter convection
        determines the rate of transport.

6.   The temperature difference between the reaction
        and the growth chambers can be made smaller when
        wider tubes are used. (Thus facilitating an
        even distribution of growth products along the
        crystallization chamber) since the gas flow
        here is the rate determining factor.

2.2.2   Growth without using a transporting agent

Crystal growth by chemical vapour transport
technique using either iodine or bromine as an agent will
give very large crystals, sometimes of more than one centi-
meter in basal extent. But these transporting agents always
contaminate the grown materials. The incorporation of the
transporting agent affects the electrical and chemical
properties of the material. Therefore, it seems that there
is a pressing need to grow as pure crystals as possible.
Hence it was considered that a method of growth which avoids
the transporting agent would be more satisfactory. Such
a method was used by Al-Hilli and Evans[26] to grow single
crystals of certain transition metal dichalcogenides. This

method of growth of crystals without a chemical transporting agent (called as direct vapour transport method) has been used in the present work to grow mixed single crystals of $MoSe_2$-MoS_2 solid solutions.

2.3 Experimental Details of Direct Vapour Transport Method

2.3.1 Dual zone horizontal furnace

Furnace is the most essential and almost basic piece of apparatus needed for this technique. Therefore it was designed to be adaptable to allow for the necessary changes of temperature gradient with different growth conditions. As higher temperatures 900 - 1140 $^{\circ}$C are required to make the vapour pressure sufficiently large to obtain a reasonable growth, the furnace must be capable of reaching the higher temperatures of the order of 1200 $^{\circ}$C and it should be able to produce temperature gradients of different magnitudes over a length of about 25 cm. To obtain the temperature stability during growth, electronic temperature controllers were used in the furnace heating circuit.

Furnace was constructed locally in our workshop 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 3 mm, imported from Koppers Fabriken Feuerfester,

Germany. Super Kanthal A-1 wire 17 SWG was wound directly

on to the furnace tube in two different regions   as

shown in Fig. 2.2. Then the tube was enclosed in the hot

face insulating brick slabs. The complete brick shell

was fully encased   in thick **asbestos**   sheets and the

entire assembly was supported in a steel frame work (Fig. 2.3).

       As the growth of sizeable crystals require

longer time to grow, the temperature in the furnace must

be accurately controlled. The power supplied to the

furnace windings was regulated by the control   circuit

shown in Fig. 2.4. The two regions of winding are provided

with independent power supplies and temperature controllers.

Transformer with 70, 80 and 100 V taps with 20 A current

capacity in secondary were used to supply sufficient power

in order to reach the required high temperature. Controllers

used are "Eurotherm controllers" which are of "fast cycling"

type switching the power on and off regularly at every 10

cycles of main frequency. The on time is continuously

variable, controlling   the power fed to the elements.

The units have "integral" and "derivative" controls to

Fig. 2.2   Kanthal A-1 wire windings for the

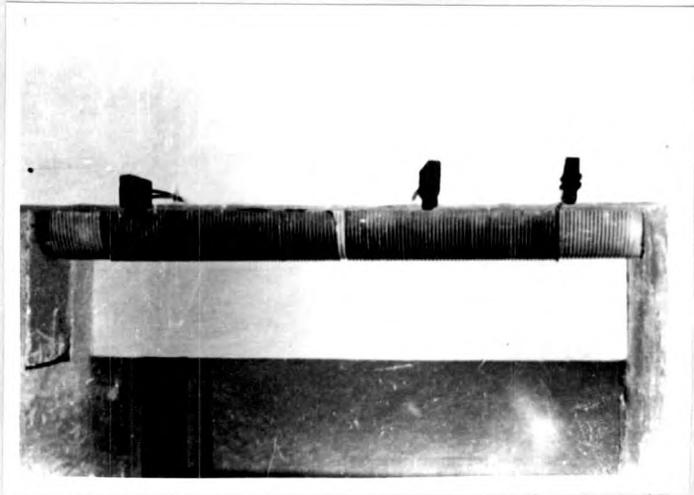two zone crystal growth furnace.

Fig. 2.2

Fig. 2.3   Schematic representation of the furnace.

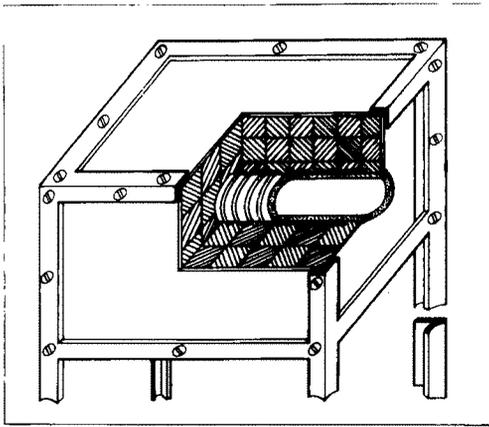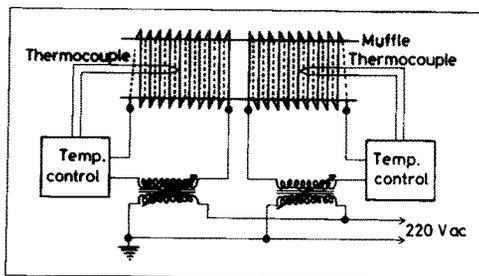Fig.2.4   Control circuit for regulating the power.

Fig. 2.3

Fig. 2.4

correct the changes in furnace temperature with no overshoot combined with cold junction compensation. This gives a stability of $\pm$ 1°C.

The fluctuations in the local electrical supply was controlled by AC voltage stabilizer with 180 to 260 V input and 230 $\pm$ 1 % output volts, of capacity 3 KVA. The output of stabilizer was fed to the primary of the transformer which heats the furnace windings and helps to maintain the stability of growth conditions. By controlling the input power to the two sets of windings 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 the Eurotherm temperature controllers 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.

2.3.2 Ampoule

The high quality fused quartz tubes have a melting point of about 1500°C. Tubes of various diameters were used for growth experiments. Tubes having internal diameter 20 mm and length 210 mm were found more suitable

for growth experiments. One end of tube was sealed and other
was drawn into a neck and joined to the other 10 mm innner
diameter quartz tube to connect it to the vacuum system for
evacuation after introducing the source material.

2.4   Crystal Growth

2.4.1   Cleaning of ampoule

First the ampoule was washed with boiled
water and detergent powder, after that it was washed with
hot mixture of conc. HNO_3 and HF (49 %) taken in equal
proportions. Then the washing was followed by double
distilled water. Again washed with a mixture of HNO_3 and
H_2SO_4 taken in equal quantities. Final washing was done
by double distilled water not less than dozen times. After
which, the cleaned quartz ampoules were transferred into
a SICO constant temperature furnace at $100^{\circ}C$ and left
overnight to make them moisture free.

2.4.2   Preparation of charge

For preparation of starting material,
powders of molybdenum, selenium, sulphur were introduced
into thoroughly cleaned quartz ampoule, 20 mm inner
diameter and 210 mm long, in stoichiometric proportions.

The materials used and their sources of supply are listed in Table 2.1. A total charge of 9-12 gm was used in each experiment. The ampoule containing the source material was evacuated to a pressure of 10^{-5} torr, proper care was taken while evacuating so that the material from the ampoule did not enter into the vacuum system. The ampoule was sealed off at the constriction 3 mm in diameter. Then the charged ampoule was/thoroughly shaken to ensure a proper mixing of the elemental powders, and the mixture was distributed along the length of the ampoule and was introduced into its furnace. The temperature of the furnace was increased in steps of 40°C per half an hour until the desired values were reached. This slow heating was necessary to avoid any possibility of explosion due to strongly exothermic reaction between the elements. The temperature of the furnace was controlled to within $\pm$ 1°C with the help of Eurotherm controllers. After 72 hours, the furnace was switched off and the ampoule was allowed to cool to room temperature. At this stage, the compound was in the form of a free flowing, shining, homogeneous polycrystalline material.

The growth procedure and conditions for the growth of MoS_xSe_{2-x} single crystals are well discussed in the next chapter.

Table 2.1

Materials from   which the crystals were grown,

with source of supply

Material	Purity (%)	Supplies
1. Molybdenum (Mo)	99.95	Koch-Light Laboratories Ltd., England.
2. Selenium (Se)	99.999	Johnson Matthey Chemicals Ltd., England.
3. Sulphur (S)	99.9999	Koch-Light Laboratories Ltd., England.

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