

C H A P T E R - 2

Growth of single crystals by chemical vapour transport technique

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2.1 INTRODUCTION

There are several methods for growing single crystals, the technique being fully described in the text books and reviews (1-11). It is well established that compounds of "transition metal chalcogenide" family are insoluble in water, which naturally prevents their growth from aqueous solutions. Following two methods of crystal growth were therefore considered.

- (i) Growth from melt.
- (ii) Growth from vapour phase.

The former was rejected because of the high melting point of the compounds involved and other complications such as, many compounds, including MoSe_2 and WSe_2 , decompose before reaching their melting points, sometimes melt incongruently or the vapour pressure is too high at melting points. Hence growth from vapour phase was found more suitable.

Crystal growth by chemical vapour transport technique using either iodine or bromine as an agent generally gives very large crystals, sometimes being more than one centimeter in basal extension. But these transporting agents always contaminate the grown materials. Therefore to grow crystals without such contamination, a method of growth which avoids the transporting agent is found to be more satisfactory.

Such a method was used by Al. Hilli and Evans (12) to grow single crystals of certain transition metal dichalcogenides (T.M.D.C's). We have also used this method for the growth of WSe_2 single crystals. However solar cells fabricated with these crystals gives very low values of efficiency.

It has been shown by different workers (13-15) that PEC cells fabricated with WSe_2 crystals grown with help of transporting agents yield the higher values of efficiency. We have therefore concentrated upon the growth of WSe_2 using various transporting agents. The results of these efforts have been described in the next chapter. A brief description of the chemical vapour transport technique is given in this chapter.

2.2 CHEMICAL VAPOUR TRANSPORT TECHNIQUE

This technique has been reported as a reliable method for the growth of TMDC Crystals (16-21). The 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 into the vapour phase at temperatures well below the melting point of the compound. Transport occurs between two zones

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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 continuous gas flow from external supplies or by its re-circulation within a closed 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 the transporting agent.

The rate of transport of the compound in gm/sec is given by Nitsche et al (14) as,

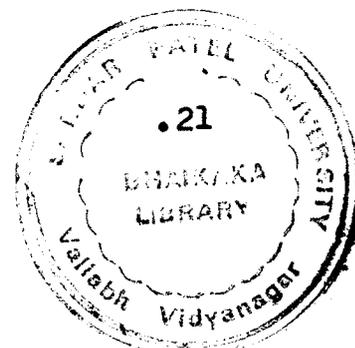
$$m = L \cdot d_p (T^h, T^c, dG, C_t) \dots\dots\dots (2.1)$$

Where,

T^h, T^c are the temperatures at the hot and cold end respectively.

d_p difference between partial pressure of the reaction product at temperatures T^h and T^c .

C_t Concentration of the transporting agent.



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

dG 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 (19) that optimum transport occurs when the reaction is not far from equilibrium, that is, d_p is a 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 (16) found a value of 5 mg/c.c 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. Three mechanisms are possible.

(a) At low pressure and with small ampoule diameter diffusion is the only important transport mechanism.

(b) As the pressure of the diameter diffusion is the only important transport mechanism.

(c) In the initial reaction equation compound + transporting agent = Reaction product. There are usually equal number of molecules in the vapour phase on each side. If this is not so, there will be a change in pressure gradient along the ampoule, and a laminar flow of the reaction product will take place.

T^i, T^m d_p depends strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature (20). Many compounds, including MoS_2 have more than one possible crystal structure, and their stability is often temperature dependent. T^m , the crystallization temperature should lie within the stability range of the required crystal type.

($T^i - T^m$) The temperature difference, is altered to control d_p , and so to vary the vapour transport rate. However, this can not be increased indefinitely without causing polycrystallization, as explained below.

Molecules condensing on to a flat surface from the vapour loose potential energy, that is they acquire a binding energy, E^1 .

However, their thermal energy gives them a probability, p^1 of evaporation.

$$p^1 \propto \exp (E^1/KT) \dots\dots\dots(2.2)$$

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

$$n = L_0 \cdot P \cdot V \quad \dots\dots\dots (2.3)$$

Where,

L_0 is the Loschmidts constant = 2.687×10^{19} per (cm³. atom).

There will be a pressure, P^1 , where the rate 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^{11} , such as a step on the crystal surface, the probability of evaporation drops. Equilibrium in such cases will occur at lower pressure, P^{11} .

If the partial pressure has a value between P^1 and P^{11} , molecules will only condense on the sites of greater binding energy E^{11} . Under these conditions crystals that have already formed will grow but no new crystals will form unless impurities bind some molecules more firmly to the amouple 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 great. Otherwise the partial pressure of the reaction

product will exceed P^1 and polycrystallization will occur.

Finally, Nitsche (17) gave following rules for the successful growth of crystals by vapour transport technique.

- a. The rate of transport must not exceed the rate of growth of the seeds.
- b. The optimum crystallization temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.
- c. The crystallization chamber should be larger in order to prevent inter growth between adjacent seeds. Asymmetric heating is therefore sometimes useful.
- d. The temperature distribution in the crystallization chamber should be as uniform as possible to avoid partial re-evaporation of already grown crystals.
- e. Well developed crystals form more easily in large diameter tubes, where transporter convection determines the rate of transport.
- f. The temperature difference between the reaction and 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 parameter.

2.3 EXPERIMENTAL DETAILS OF CHEMICAL :

VAPOUR TRANSPORT TECHNIQUE :

2.3.1. DUAL ZONE HORIZONTAL FURNACE :

The first and the foremost basic essential piece of the apparatus required for chemical vapour transport method is a furnace capable of providing an appropriate temperature gradient all over the ampoule. The furnace must be capable of reaching higher temperatures of the order of 1200°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 circuits. Furnace was constructed in our workshop by using a special Sillimanite threaded tubes (grade KR 80 GAHG), closed at one end, 45 cm in length, 7 cm outer diameter 5.6 cm inner diameter with threaded pitch 0.3 cm, imported from Koppers Fabriken Feuerfester, Germany. Super Kanthal A-1 wire 17 SWG was wound directly on to the furnace tube in different regions. 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. 2.2).

As the growth of sizeable crystals require longer time the temperature in the furnace must be accurately controlled. The power supplied to the furnace windings was regulated by the controlled circuit (Fig .2.3). 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 capacity in secondary were used to supply sufficient power in order to achieve the required high temperature. Controllers used were "Eurothem^A Controllers" which were of "fast cycling" type switching the power on and off regularly at every 10 cycles of mains frequency. The on time was continuously variable, controlling the power fed to the Kanthal A-1 windings. The control units have "integral" and "derivative" controls to correct the change in furnace temperature with no overshoot. Combined with cold junction compensation, this gives a stability of $\pm 1^{\circ}\text{C}$.

The fluctuations in the local electrical supply were controlled by using an A.C. Voltage stabilizer with 180 to 260 V input and $230 \pm 1\%$ output volts of capacity 3 KVA. The output which was fed to the primary of the transformer heats the furnace windings and helps to maintain the stability of growth conditions.

By controlling the input power to the two steps of windings a required temperature gradient could be established across the length of the work tube in the proper temperature range. Thermocouples used were pt (13%) Rh-Pt, and the Eurotherm temperature controllers were calibrated for the above thermocouples. It was seen that thermocouples were stable over the prolonged use in the furnace and they were supported within the furnace tube itself, showing the furnace tube temperature.

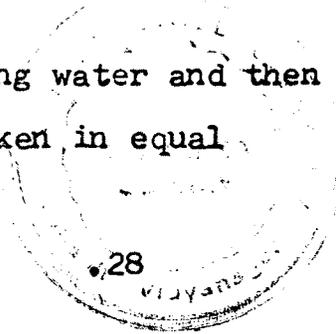
2.3.2. AMPOULE :

High quality fused quartz tubes used in the growth experiments have a melting point of about 1500°C. Tubes of various diameters were used. Tubes with internal diameter of 2.5 cm and length 22 cm were found to be more suitable for the present growth experiments. One end of the tube was sealed and other was drawn into a neck joined to a silicon tube of 1 cm inner diameter to connect it to the vacuum system for evacuation after introducing the source material. An ampoule after sealing has been shown in Fig.2.4.

2.4. CRYSTAL GROWTH

2.4.1. CLEANING OF THE AMPOULE :

First of all the ampoule was washed with boiling water and then with boiling concentrated HNO_3 and HF (49%) taken in equal



proportion (i.e. 1:1). Afterwards it was washed with distilled water. A further washing was carried out with concentrated H_2SO_4 and HNO_3 in equal proportions followed by a final washing for about ten to twelve times with doubly distilled water. The ampoule was then kept in a SICO constant temperature furnace at $100^\circ C$ and left for overnight heating to make it moisture free.

2.4.2. CHARGE PREPARATION :

For the charge preparation the required materials (Table 2.1) for growth are 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 is then connected to a vacuum system and precaution being taken that the vacuum be brought so slowly that none of the materials from the ampoule can enter the vacuum system. A total charge of 4-6 gm was used in each experiment. When the vacuum is being reached, the ampoule is tapped slowly so that any air between the particles of the materials is removed, when a vacuum of the order of 10^{-5} torr is reached, the ampoule is sealed off at the neck.

The sealed ampoule with the elemental powder is shaken thoroughly to ensure proper mixing of the contents. The mixture is then distributed uniformly all over the length of the ampoule.

The ampoule is thus ready for keeping it in the furnace.

After keeping the ampoule at an appropriate place in the horizontal furnace, the temperature is slowly increased. The temperature and the period for which the ampoule is kept in the furnace depends upon the material which is being grown. The slow heating is necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements. Comparatively large size of the ampoule and well uniform distribution of the powder will minimise the temperature rise to prevent an explosion. After specific time of heating at the required temperature the furnace is switched off and after bringing it to room temperature it will be seen that the ampoule has a fine free flowing shiny homogeneous polycrystalline material.

Just as the specific conditions of temperature and reaction time are different for charge preparation the same way actual growth procedure also varies from material to material. The methods of crystal preparation used by some of the workers (10-12, 16-20) are found to yield crystals of very high crystallographic quality.

The growth procedure and conditions for the growth of WSe_2 single crystals are well described and discussed in the next chapter.

TABLE - 2.1
MATERIALS FOR WHICH THE CRYSTALS WERE GROWN
WITH SOURCE OF SUPPLY

Material	Purity (%)	Supplier
Tungsten (W)	99.999	Koch-light Laboratory Ltd., England
Selenium(Se)	99.999	Johnson Matthey Chemicals Ltd., England
Selenium tetrachlo- ride (SeCl ₄)	-	E.Merck., Germany
Tellurium tetrachlo- ride (TeCl ₄)	-	E.Merck., Germany
Bromine (Br ₂)	-	Sameer Tech. Chem., Baroda

REFERENCES

1. "Crystal growth" 1949 Disc Faraday Soc. 5.
2. Buckley, H.E. 1951
Crystal Growth, John Wiley and Sons, New York.
3. Lawson, W.D. and Nielsen, S 1958,
preparation of single Crystals,
Butterworths Scientific Publ. London.
4. Smakula, A., Einkristalle, Wachstau,
Herstellung, Anwendung,
Springer Verlag, Berlin 1962.
5. Lawson, W.D., Nielsen, S. and Gilman, J.J.
(ed) 1962.
6. White, E. A.D. 1970
Brit. J. Appl. Phys. 25, P. 151.
7. Laudise, R.A. 1970,
The Growth of single crystals, prentice-Hall
Inc., New Jersey.
8. Henisch, H.K. 1970
Crystal growth in Gels, The Pennsylvania State
University Press, University park, London.
9. Parker, R.L. 1970,
Solid State Phys. 25, P.151.
10. Korger, F.A. 1973,
"The Chemistry of Imperfect Crystals"
2nd Revised Edition, Vol.1,
preparation, purification, crystal growth and phase
theory, North-Holland publishing Co., Amsterdam -
London, American Elsevier publishing Co., Inc. New York.
11. Mullin, J.W. 1972
Crystallization, Butterworths Scientific Pub. London
2nd Ed.

12. Al. Hilli, A.A. and Evans, B.L. 1972,
J. Crystal growth, 15, 93.
13. Parkinson B.A., Furtak T.E., canfield D,
Kain K, and Kline G, 1980,
Faraday Discuss Chem., Soc., 70, 233.
14. Ren-Fu. F.Fan, Henry S. White, Bob Wheeler
and Bard J. Allen, 1980,
J.Electrochem Soc., 127, 519.
15. Prasad G, and Srivasatava O.N. 1988,
J. Phys. D. Appl. Phys. 21, 1028.
16. Nitsche, R. 1961
J. Phys. Chem. Solids 17, 163.
17. Nitsche, R., Boelsterli, H.V. and
Lichtensteiger, M. 1961
J. Phys. Chem. Solids, 21, 199.
18. Brixner, L.H. 1962,
J. Inorg Nucl Chem. 24, 257.
19. Schafer, H. 1964,
"Chemical Transport reaction"
Academic press, New York.
20. Nitsche, R. 1967,
"Crystal growth" Editor H.S. peiser
pergamon oxford, P-215.
21. Nitsche, R. 1967,
"Proceedings in International conference on
crystal grwoth" 1966, Boston.
J. Phys. Chem. Solids Suppl. 1, 215.

CAPTIONS OF THE FIGURES

- Fig. 2.1. : Illustration of the cyclic process of chemical vapour transport in a closed system.
- Fig.2.2. : Schematic representation of the furnace.
- Fig. 2.3. : Control circuit for regulating the power
- Fig. 2.4. : A sealed ampoule with 22 cm length.



Growth by iodine vapour transport

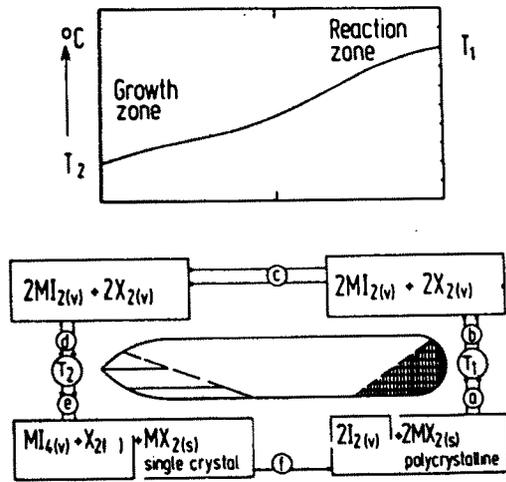


FIG. 2.1

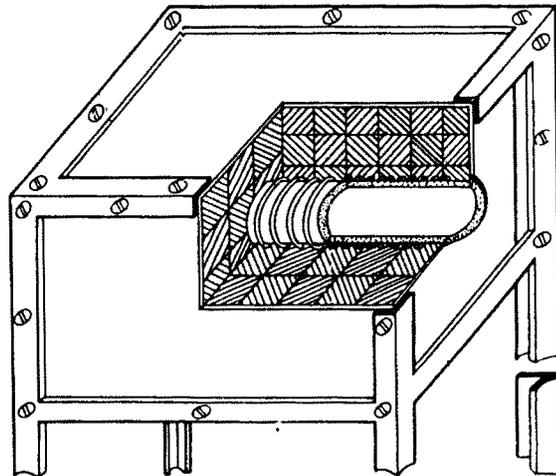


FIG. 2.2

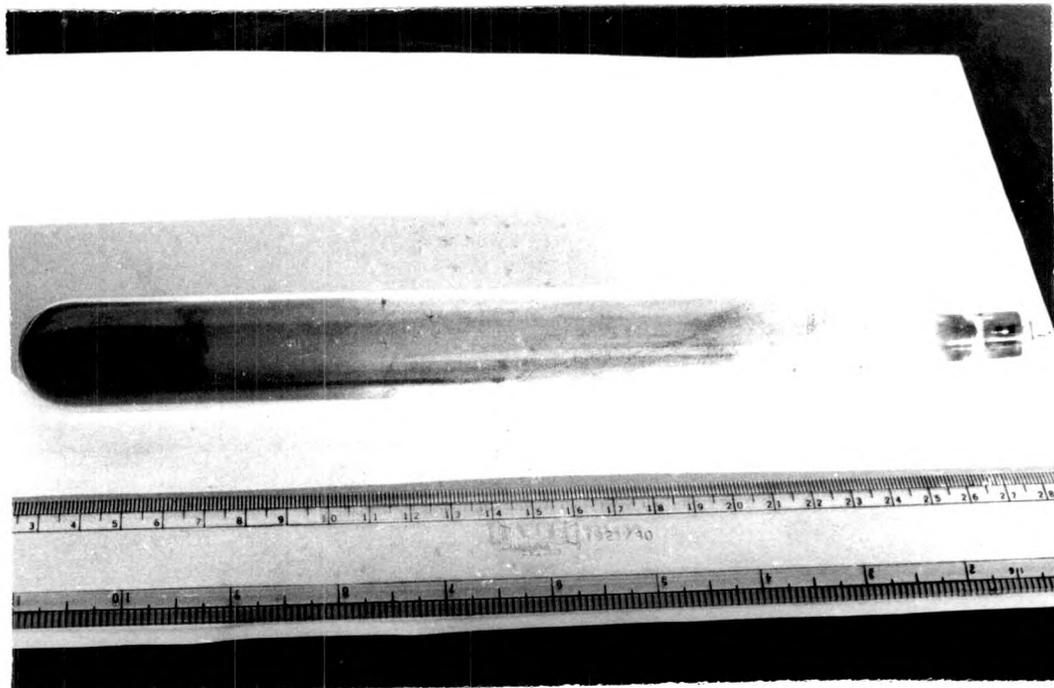
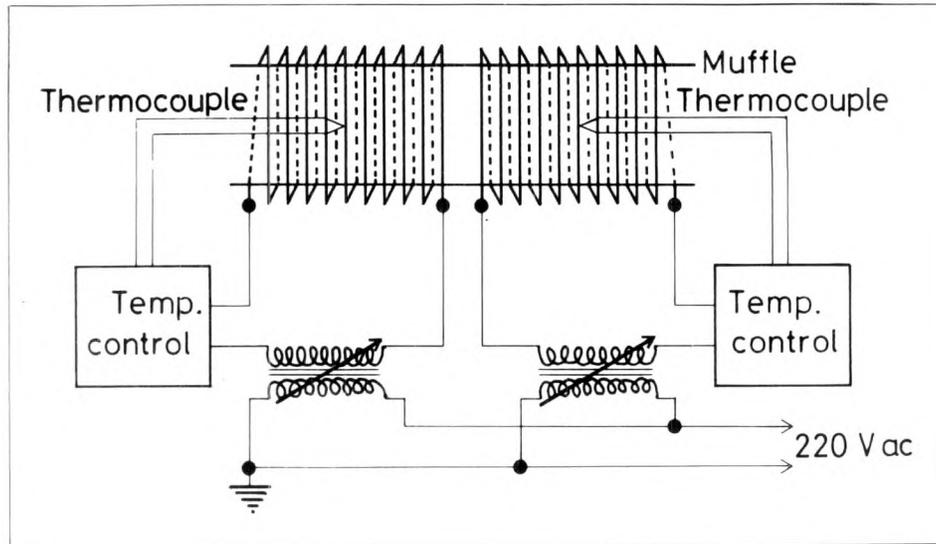


FIG-2.3
FIG-2.4