CHAPTER 4

GROWTH OF SINGLE CRYSTALS BY A VAPOUR PHASE METHOD

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4.1   Introduction

       The growth of crystals depends on their various parameters, like melting point, vapour pressure and solubility in water. Hence, in the light of this only, different methods of crystal growth, such as,

(i)   growth from melt,

(ii)   growth from vapour phase, and

(iii)   growth from aqueous solution

were considered.

       Now, so far as the growth of crystals of transition metal dichalcogenide group is concerned, the methods of growth from melt as well as growth from

aqueous solution will be highly impracticable, because
the compounds of transition metal dichalcogenide
group are insoluble in water and moreover these techniques
fail because of high melting points or prematured
decomposition. The only alternative or possible method
for growing these crystals, is, therefore, the method
of growth from vapour phase. This method can also be
divided into two :

(i)   chemical vapour transport method, and

(ii)   direct vapour transport method.

First, the method of growth by chemical vapour
transport is discussed.

4.2   Vapour Growth Technique

4.2.1   Chemical vapour transport method

New theoretical attempts of vapour
transport of solid have been given by Lever[1,2],
Mandel[3,4] and Arizumi and Nishinaga[5]. Kalidas has
shown that it is possible to grow crystals up to several
cm^3 in size by chemical transport under well controlled
nucleation conditions at small supersaturation
(Cd_4GeS_6)[6] and from seeds $(ZnSe)$[7]. The transport
of solid matter through the various phases via gaseous
intermediates, utilizing the temperature dependence of

heterogeneous equilibria (chemical transport reactions), has gained considerable attention in recent years.

Originally used by Van Arkel and De Boer[8] for the preparation of high purity refractory metals (iodide metals), transport reactions have been studied systematically by Schafer and coworkers[9]. It enabled investigators to grow single crystals of substances hitherto known as "difficult materials".

On the solid ground, thus, the chemical vapour transport method has been reported as a reliable one for growing metal dichalcogenide single crystals[10-15]. This technique relies on a chemical reaction between the compound to be crystallised and 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 of different temperatures. Usually the initial reaction occurs at the high temperature and is reversed at the low temperature to deposit molecules of the compounds at the most favourable crystalline sites. Initially, random deposition occurs until seed crystals are formed. Thereafter, growth should only occur on these seeds, and large single crystals should be formed.

The transport of the reaction product
in the vapour phase can be achieved by a continuous
gas flow from external supplies, or by its recirculation
within a closed tubular ampoule.

The rate of transport of the compound
in gas/sec. given by Nitsche et al.[11] is,

$$m = L. dp (T', T'', dG, Ct) ..$$ (4.1)

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

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

dG   is the Gibbs free energy change in
the reaction,

Ct   is the concentration of transport
agent,

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

These parameters of the transport equation (4.1) have
the following significance.

dG

It has been found by Schafer[13] that optimum transport occurs when the reaction is not far from equilibrium, that is, dp is a maximum for values of dG not far from zero. For chalcogenides, the halogens are most commonly used as transporting agents, out of these, iodine gives the lowest dG value and is usually the best choice. However, for some compounds, bromine gives better results.[12]

Ct

Nitsche[15] found a value of 5 mg/cc for Ct 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.

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

2. As the pressure or the diameter is increased

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

3.   In the initial reaction   equation,
        compound + transporting agent = Reaction
        products.

        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', T"

        dp depends strongly on the temperature
gradient along the ampoule and to a lesser extent on
the absolute temperature.[15]

        Many compounds, including TaS_2, have more
than one possible crystal structure, and their stability
is often temperature dependent. T", the crystallization
temperature should lie 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 onto a flat surface
from the vapour loose potential energy, that is, they
acquire a binding energy, E'. However, their thermal
energy gives them a probability, P', of evaporation.

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

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.).

$$n\ =\ L_o\ \ P.\ V$$

$$L_o\ =\ Loschmidts\ constant$$

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

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

In reality, when a molecule condenses
onto a crystal, it will tend to migrate over the
surface before evaporating. 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 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. If it is, the partial pressure of the reaction product will exceed P' and polycrystallization will occur.

Finally, Nitsche et al.[11] gave the 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 crystallisation chamber should be larger
        in order to prevent intergrowth between
        adjacent seeds. Asymmetric heating is some-
        times useful.

(d)   The temperature distribution in the crystalli-
        sation 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 the growth chambers can be made smaller
        when wider tubes are used (thus facilitating
        an even distribution of growth products along
        the crystallisation chamber) since the gas
        flow here is the rate determining parameter.

4.2.2   Growth without using transport agent

Crystals grown by chemical vapour technique
are sometimes several mm square in size, eventhough there
is evidence that they suffer from the obvious dis-
advantage of contamination by the transporting agents
which in the present case of TaS_2 were either bromine

or iodine[16-20]. The possibility of the entry of
bromine or iodine to the crystal lattice cannot be
ignored, and as a consequence of this the electrical
and chemical properties of the crystal will be
affected. Since the aim of growing TaS_2 single crystals
was to obtain crystals which are as pure and defect
free as possible, the method of growth without using
transport agent was adopted. Al-Hilli and Evans[21]
used such a method in growing single crystals of
certain transition metal dichalcogenides. This method
of growth of crystals without a chemical transporting
agent will be called as sublimation method or the
direct vapour transport method in what follows.

4.3   Experimental Set Up of Direct Vapour
       Transport Method

4.3.1   Two-zone horizontal furnace

        The first and the formost basic
essential piece of the apparatus required for this
technique is a furnace fulfilling the appropriate
temperature gradient all over the ampoule. As
compared to chemical vapour transport method, here
in the sublimation technique, higher temperatures
are required to raise the vapour pressure sufficiently

large for obtaining reasonable rate of growth. The
furnace should, therefore, be capable of reaching
higher temperatures with required temperature
gradients over a length of about 25 cms. To ensure
temperature stability during growth, electronic
temperature controllers were used for the furnace.

Economically it was considered
advisible to construct such experimental furance
locally in our workshop rather than purchasing one
commercially with the same specifications. In
designing the furnace, special sillimanite threaded
tubes (Grade KR 80 GA (HG)) closed at one end and
having 45 cms. length, 70 mm outer diameter, 56 mm
inner diameter and a thread pitch of 3.0 mm, imported
from Koppers Fabriken Feuerfester Erzeugrisse
GmbH, Germany were used. Super kanthal A-1 wire of
17 gauge (SWG 17) was wound directly on to the
furnace tube in two different regions in the manner
indicated in Fig. 4.1. The sillimanite furance
tube with kanthal A-1 winding was then enclosed in
the hot face insulating brick slabs specially constructed
locally. The complete brick-shell was, then fully
encased in thick asbestos sheets, and the entire
assembly was supported in a steel framework as shown

in Fig. 4.2.

As sizeable crystals require considerably
long time period to grow, an accurate device to control
the temperature in the furnace is a must. The control
circuit used for regulating the power supply is shown
in Fig. 4.3. The two regions of winding have been
provided with their own independent power supplies
and temperature controls, 20 ampere transformers with
240 volts in primary and with 70, 80 and 100 volts in
secondary were used to supply sufficient power to reach
the required temperature quickly. Controllers used are
"Eurotherm controllers" which are of the "fast cycling"
types, switching the power on and off regularly at every
10 cycles of main frequency. The "on" time is conti-
nuously variable, controlling the power fed to the
kanthal A-1 windings. The control units have "integral"
and "derivative" controls to correct changes in
furnace temperature with no overshoot. Combined with
cold junction compensation this gives a stability of
$\pm 1^0$ C.

Generally one observes a lot of
fluctuations in the local power supply and obviously
this will not allow the conditions for the growth to
remain uniform. This difficulty was overcome by using

voltage stabiliser with 180 to 260 V input and 230 $\pm$ 1 % output volts of capacity 3 KVA. The output of this was fed to the primary of the transformer windings to ensure and maintain stable growth conditions during the growth.

By controlling the input power to the two sets of windings a required temperature gradient could be established across the length of the work-tube. The furnace was found to be capable of giving wide range of temperature gradients as and when required as per the experimental set up.

The thermocouples used were platinum (Pt) 13 % Rhodium Platinum (Rh-Pt). Actually the "Eurotherm" temperature controllers used in the furnace were calibrated for these thermocouples. It was observed that the thermocouples were quite stable over the prolonged use of the furnace. The thermocouples were supported within the furnace tube itself so that they follow the furnace tube temperature.

4.3.2   Ampoule

Transparent quartz tubes, of high purity and quality, possessing high melting point were used as ampoules. The tubes used were of various internal and external diameters. However, tubes with

internal diameter of 22 mm and length 215 mm were found
to be most adequate for the growth experiments under
study. One end of the tube was sealed and other drawn
into a neck and joined to a silicon tube of 10 mm
inner diameter to connect it to the vacuum system for
evacuation after introducing the source material.

4.4 Crystal Growth

4.4.1 Cleaning the ampoule

The ampoule was first washed with boiled
water and then with boiling concentrated HNO_3 and HF
(49 %) taken in equal proportions i.e. (1 : 1). The
ampoule was then washed with distilled water. A further
washing was carried out with concentrated H_2SO_4 and
HNO_3 taken in equal proportions, followed by a final
washing for about half a dozen to a dozen times with
doubly distilled water. The ampoule was then kept in
a SICO constant temperature furnace at about 100° C
and left over night for drying. It was then connected
to a vacuum system and heated up for removing the
adsorbed gases.

4.4.2 Compound preparation

For the compound preparation the
required materials for growth are taken in a stoichiometric

ratio and filled up in a transparent quartz ampoule
duly cleaned and dried by the process explained above.
The ampoule containing the source materials 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 entre the
vacuumsystem. When the vacuum is being reached, the
ampoule may be tapped slowly so that any air between
the particles of the materials may be 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 should be 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 two-zone horizontal furnace, the temperature
is slowly increased. The temperature upto which 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, shining homo-
geneous polycrystalline material.

4.4.3 Growth procedure

Just as the specified conditions of
temperature and reaction time are different for
compound preparation, in the same way actual growth
procedure varies from material to material. The
methods of crystal preparation used by some of the
workers[10-13,22] are found to yield crystals of very
high crystallographic quality.

The growth procedure and conditions
for the growth of TaS_2 single crystals are well
described and discussed in the next chapter.

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Captions of the figures

Figure 4.1   Kanthal A-1 wire windings for the
             two-zone crystal growth furnace.

Figure 4.2   Schematic representation of the
             furnace.

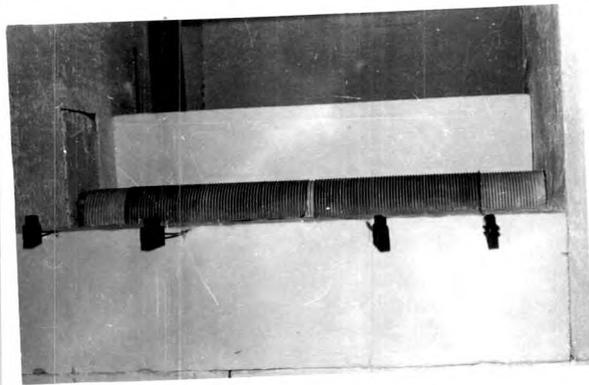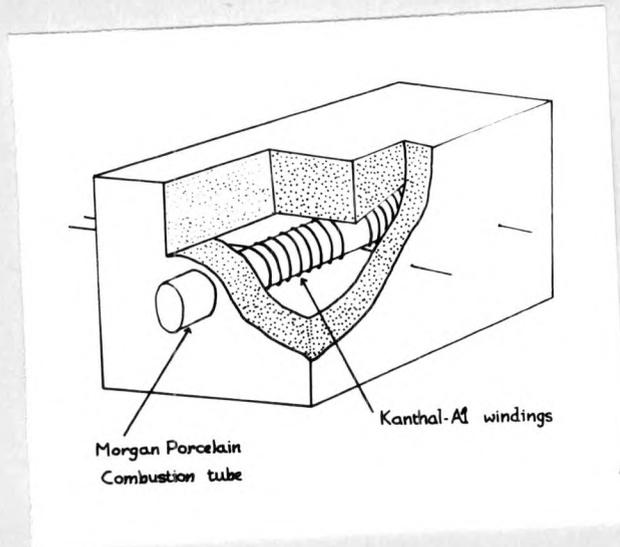Figure 4.3   Control circuits for regulating
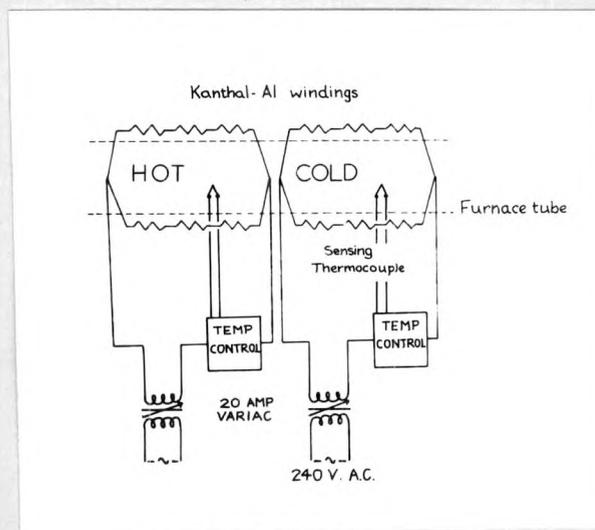   the power.

Fig. 4.1

Morgan Porcelain
Combustion tube

Kanthal-A1 windings

Fig. 4.2

Kanthal- Al windings

HOT   COLD

Furnace tube

Sensing
Thermocouple

TEMP
CONTROL   TEMP
CONTROL

20 AMP
VARIAC

240 V. A.C.

Fig. 4.3