



## CHAPTER II

### LIQUID PHASE EPITAXY EXPERIMENTS

#### The Design and Construction of the Vertical Liquid Phase Epitaxy System (VLPE)

Since the epitaxial growth process requires that the arriving Sn atoms find their attachment positions on the host lattice sites in order to assume the crystallographic continuity the surface of the substrate must be free of obstructing or foreign atoms. The key to successful epitaxy therefore requires that the substrate surface be clean before entering the system and kept clean until the epitaxial process starts. The substrate preparation is discussed in the next section. The epitaxy system itself is designed to accept the cleaned substrate, provide the ambient to maintain its cleanliness or to further clean it. The system also provides the source material (Sn) for epitaxy and means to manipulate the growth process.

In order to achieve the above the VLPE system is designed and constructed as schematically shown in Fig. 2. Ultra-clean  $H_2$  environment is provided within the system by means of a hydrogen generator (Milton-Roy Mark V), a purifier (Matheson HP 8363) and a gettering bubbler containing a mercury-tin solution saturated at room temperature. The growth system consists of the upper air-lock/sample holder, the gate valve, and the lower growth tube.

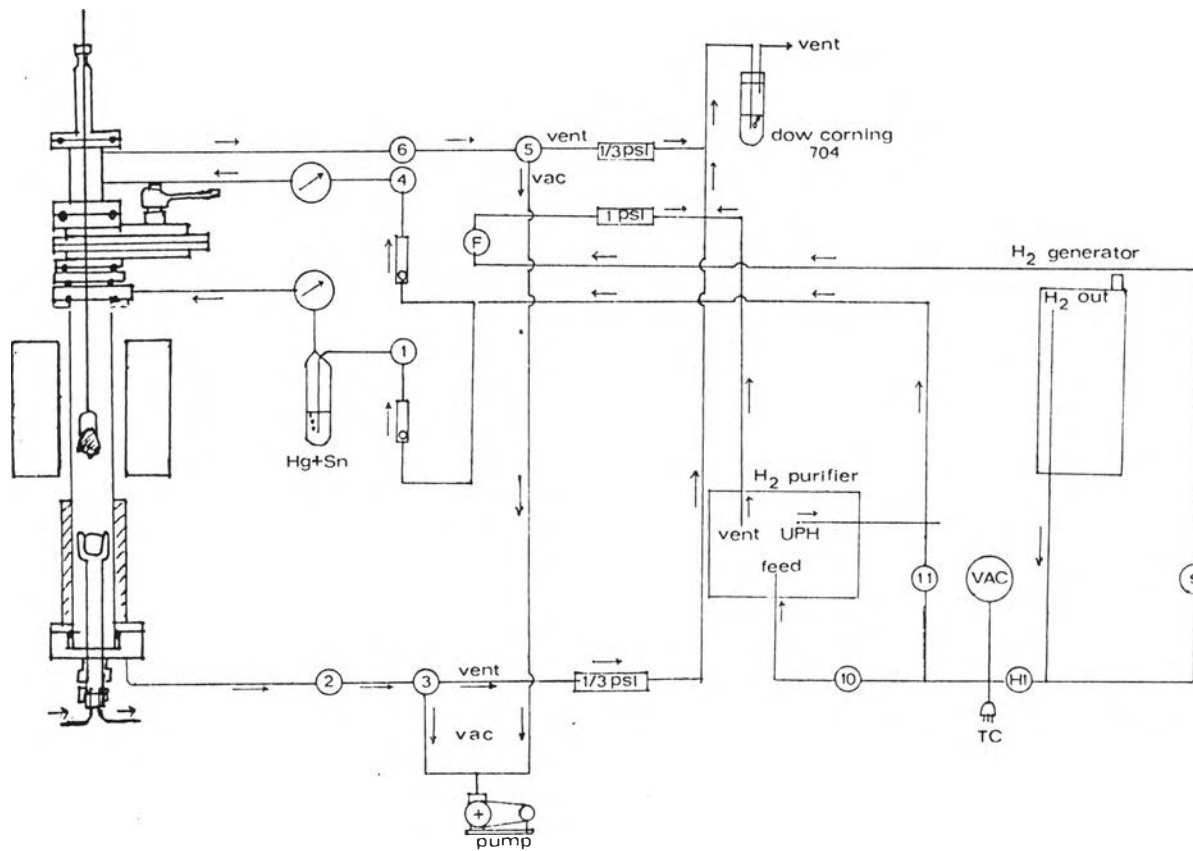


Fig. 2. Schematic diagram of the VLPE system and the more detailed of the growth parts as shown in the next page,

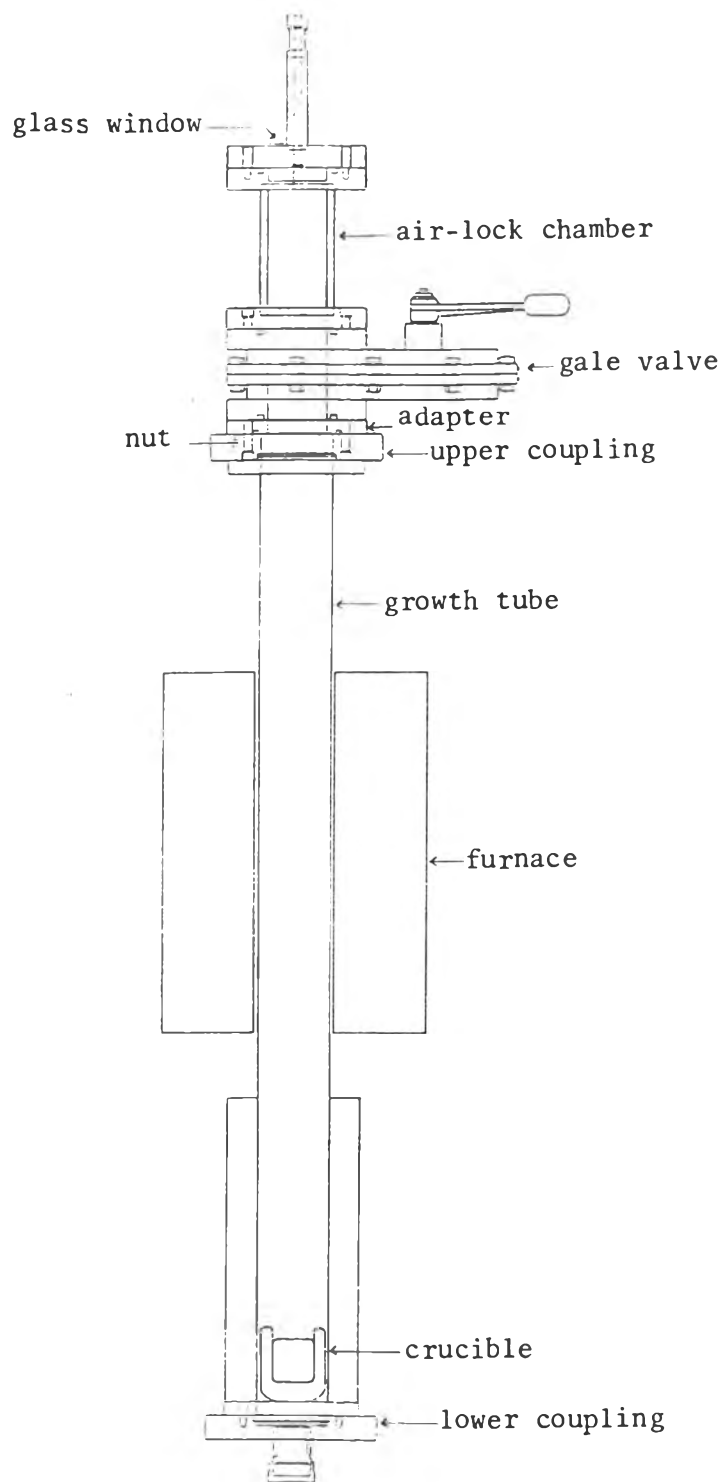


Fig. 2. (Continued)

The upper air-lock/sample holder portion would hold the vertical sample holder rod, which could be moved up and down through an air-tight seal at the top end. The main body of this part accommodates the sample size up to 2". The lower end of the sample holder rod is designed to grab a sample wafer at three parts. It is designed to minimize the thermal mass as well as thermal conduction, so that (as will be evident later) it minimally disturbs the growth process. It is made of quartz which would least likely contaminate the system.

The gate valve for the system used in this thesis work is a 2 1/2" opening sliding gate valve. A later system has a larger chamber integrating the valve and the air-lock so that two samples can be mounted to facilitate sample in, sample out sequence with less turn-around time.

The lower part is the business part of the growth system. The growth tube is made of quartz, 2 1/4" I.D., and is approximately 80 cm. long. The lower end seal also provides support for the melt crucible, which is mounted at approximately 10 cm. above the seal. The upper part of the growth tube, below the gate valve, is enclosed in a furnace which would provide a controlled heating of the tube, up to 800 °C if desired. The heating is used to clean the InSb while the latter is in ultra pure H<sub>2</sub> atmosphere.

Since the growth temperature is to be below room temperature the growth tube's lower section is insulated and the melt crucible is designed such that coolant liquid could be pumped in and out so that

the melt temperature is controlled. The crucible, also made of quartz, contains up to 40 cc. of Hg. The temperature can be controlled to  $\pm 0.02^\circ \text{C}$ , as measured by a thermocouple pushed through another, concentric, bottom seal to touch the wall in contact with the melt.

The melt is Hg which is saturated with Sn at the growth temperature. The means to load Hg into the crucible and to saturate it with Sn require special tools made of quartz. The importance of the design and the procedure to accomplish the Hg loading and saturation cannot be over emphasized; indeed the degree of the limited success in epitaxy so far could be attributed to how clean the initial melt is. The presence of a slag layer, even as little as to be invisible, would contaminate the surface of the InSb substrate as the latter is submerged for epitaxy. We will return to the Hg loading and saturation procedures later.

The details of the system operation and maintenance are given in Appendix. These include the cleaning procedures for the various parts and the assembling of the latter, the start-up procedures and the mechanical operations such as valve open/ close sequences. Some of these detailed operations may at first appear as black-art tedium but are actually based on sound scientific rationales. For example, the growth and/or air-lock chamber after exposure to air would have to be evacuated and refilled with  $\text{H}_2$  seven times. If the "vacuum" state of the system is a fraction  $p$  of the operating pressure which is approximately one atmosphere, then the seven cycles represent a

reduction of contaminant gases by a factor  $p$  to the seventh power. Certainly  $p$  can be made less than  $10^{-1}$ , which ensures the high purity  $H_2$  state in the system.

Much of the metal parts of the gas handling portion of the system (valves, tubings and fittings) are made of brass and copper instead of stainless steel due to the budget constraints. In retrospect this is proven to be a false economy. The presence of Hg vapor in the system, however minute, leads to gradual corrosion of these parts. It is also believed that some oxygen may be slowly released from the inner wall of the copper tubing. A new epitaxy system will be built exclusively using stainless steel parts.

#### Substrate Preparation

In order to obtain good epitaxial growth, "in situ" cleaning substrate procedures are necessary. The InSb wafers have been used as a substrate for liquid phase epitaxy growth in the heteroepitaxy of  $\alpha$ -Sn, are abraded and polished which normally have many crystalline defects occurred from the production processes. A necessary prerequisite for good epitaxial growth is a substrate surface which is smooth and clean on an atomic scale. The chemical treatments include wet etching which is usually used in surface preparation for liquid phase epitaxy growth. The chemical etching methods rely on an oxide film to passivate the surface which is then desorbed by "in situ" heating in reducing atmosphere. In order to be effective, the passivating film should have a low carbon sticking coefficient, be

thick and uniform on an atomic scale in order to encapsulate the substrate, have a high vapor pressure at some temperature less than the substrate melting temperature.

Normally, the etchant  $\text{HNO}_3$  : HF (3:1 in volume conc.) is used for fast etching and the etchant lactic acid :  $\text{HNO}_3$  (10:1 in volume conc.) is used for slow etching or polishing treatment of InSb.(22) The etchant lactic acid :  $\text{HNO}_3$  : HF (25:4:1 in volume conc.) was used in this experiment, which is the same as the chemical treatment of InSb surface before loading into MBE (molecular beam epitaxy) chamber in the growth of Sb and InSb on InSb substrate by MBE.(21) This etchant is the mixture of polishing etchant and fast etchant. When two etchants were poured together and let stand there result two solution layers in a ratio of about 1:5 by volume due to different specific gravity values. The "one" part is above on the "five" parts, or the fast etchant is above the slow etchant. It is necessary to shake the etch mixture well before use.

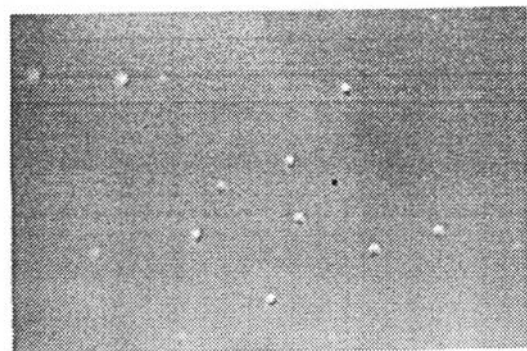
The stagnant etching method was used by careful slow dipping the substrate into the etchant to minimize swirls. The sequences of etching apparently start with fast etching of the surface oxides whose product rises. The lower etchant (polishing etch) performs later, its etching rate is controlled by atomic diffusion, best without convection of etchant. The etching time is long and without convection, the smooth surface obtains. Stop immediately the etching by dunking the small etch "thimble" into a large "bucket" in deionized  $\text{H}_2\text{O}$  (18 megohm-cm resistivity, Millipore products) to minimize the effect of convection on substrate surface. Rinse with running

deionized  $H_2O$  continuously for neutralization solution which can be investigated by indicator pH paper. And dried with  $N_2$  jet in laminar air filtered box ( $0.1 \mu$  filter for  $N_2$  jet) as fast as possible to minimize the dirt's attachment to the substrate surface. After that, the substrate is to be loaded into the air-lock chamber, which is to be evacuated and refilled with UPH seven times, before opening the gate valve and lowering it to the middle of the growth tube. (See Appendix, which also describes the furnace to heat clean of the surface of InSb to desorb the passivating oxide layer before the LPE growth).

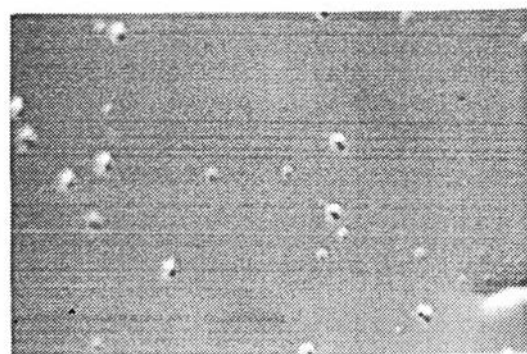
The last step in this cleaning procedure, i.e. the rinsing with deionized  $H_2O$ , 18 megohm-cm resistivity, is to passivate the surface by forming an oxide film to be desorbed by "in situ" heating at about  $475^\circ C$  in reducing UPH atmosphere. This is the new technique which was developed in this thesis. The InSb substrates were etched in lactic acid:  $HNO_3$  : HF (25:4:1 in volume conc.) for various times such as 5, 10, and 15 minutes. The surface is examined under an optical microscope (magnification 200 x) as shown in Fig. 3 to select the optimum etching time, which is found to be 10 minutes. Fig. 3 a shows the surface after 5 minutes etching time. The 10 minutes etching time is judged most suitable because the etch pits are not too deep and the surface is very smooth as shown in Fig. 3 b. Fig. 3 c shows the etch pits after 15 minutes etching time. They are too deep.

After heat cleaning the InSb substrate "in situ" in UPH atmosphere for 45 minutes to make sure that the oxide film is desorbed, the clean surface will appear colourless, mirror-like shiny

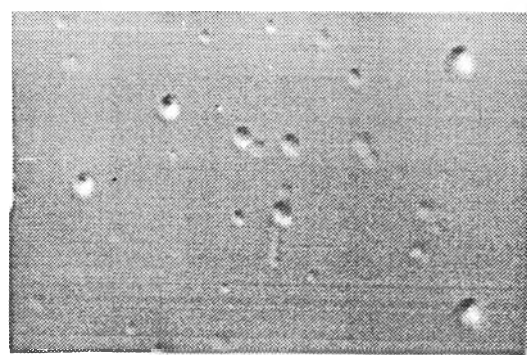




(a)



(b)



(c)

Fig.3 Surface of (111)B InSb after etching in Lactic :  
 $\text{HNO}_3$ : HF (25:1:1 conc. in volume) for 5,10, and 15  
minutes in (a), (b), and (c) respectively. Observed  
with optical microscope (200X).

when observed through the growth tube under tungsten lamp illumination. An unclean surface may appear yellow colour, in which case the sample should be unloaded and recleaned. It also indicates that the atmosphere is not clean enough. In principle in the cleanest available UPH atmosphere the impurity contents correspond to less than  $10^{-11}$  which or about  $10^9$  collisions/cm<sup>2</sup> /sec. of the impurity gas on a surface. In such UPH atmosphere it would take  $10^6$  seconds to form a monolayer of impurities on a completely clean InSb surface, or about  $10^{-5}$  monolayer a second.(23) The system should be leak checked and cleaned before an experiment restart. Even so, purging of impurities outgassed from the wall may require a very long time before the system becomes sufficiently clean again.

#### Melt Preparation

The crucible which is made from quartz can contain up to 40 c.c. of melt. The temperature can be controlled accurately to  $\pm 0.02$  °C during the saturation and the LPE growth. The importance of the procedure to accomplish the Hg loading and saturation with Sn cannot be over-emphasized, indeed the degree of the limited success in epitaxy so far could be attributed to how clean the initial melt is. The presence of a slag layer, even as little as to be invisible, could contaminate the surface of the InSb substrate as the latter is submerged for epitaxy. This section will discuss in details the melt preparation which involves feeding mercury into the crucible, saturation of Sn in mercury and the cleaning technique of the starting materials and container parts.

It is well known that(24) "dirty" mercury "tails" on glassware. But it is also true that as little as 0.1 ppm of any base metal causes a detectable scum on the surface of the mercury, presumably due to oxidation of the base metal. Pure mercury has a perfectly shiny surface appearance. The scum can be removed mechanically by running mercury through a succession of fine glass capillaries (small hole separating funnels) until the last capillary remains clean. Care should be taken to avoid contamination with dust at all stages of preparation. This method was called capillary filtration.(25)

The pure mercury after the scum removal is loaded into the crucible in the LPE system through the load lock- chamber with the containers are shown in Fig. 4. The Hg to be feeded is poured into the quartz separating funnel which the valve is made from teflon. The teflon valve fits to the quartz housing of the funnel and eliminates the use of lubricated the vacuum grease which would contaminate the mercury, and is shown in Fig. 4 a. The output end of the quartz funnel inserts into the teflon separating funnel as shown in Fig. 4 b. The output end of this teflon separating funnel connected to the upper end of the 1/4 inch quartz tube (as shown in Fig. 4 c) which is inserted through the O-ring seal guide of the load-lock chamber. This 1/4 inch quartz tube is about 1 meter long. The mercury flows down inside this quartz tube by gravity into the bulb (1 cm in diameter) at the lower end, as shown in Fig. 4 d, and which is in the crucible to prevent the Hg drops from jumping out of the crucible during feeding. The bottom of the bulb drains through a small-bore "C" shape tube as shown in Fig. 4 e. When the amount of Hg in the bulb is such that the

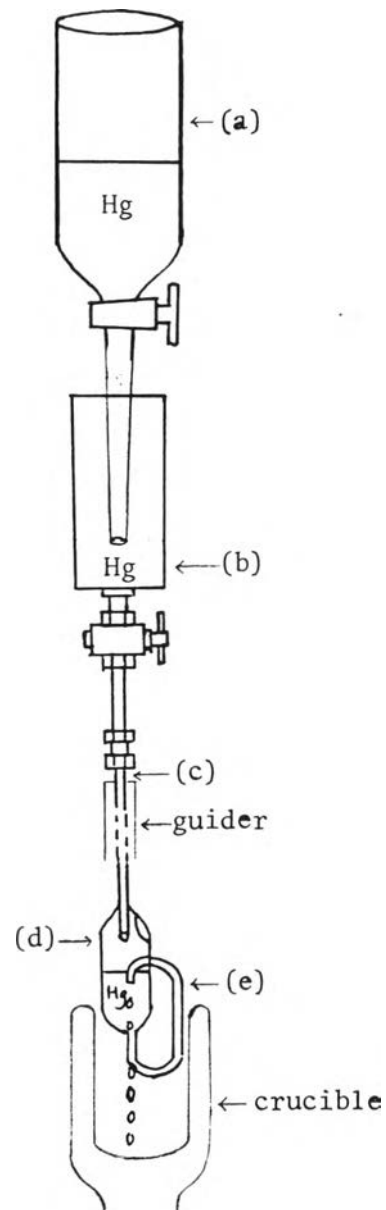


Fig.4 Arrangement of three parts of feeding container.

Hg level in the bulb is above the uppermost part of the "C" shape tube, the Hg can flow into the crucible but only if the level is maintained higher than the exit end of the tube. In this way the slag, if any on the surface of the Hg in 4 d is kept from reaching the crucible. The Hg that reaches the crucible is thus exposed only to the UPH atmosphere and appears free from visible slag as shown in Fig. 5.

These loading container parts which are made of quartz and teflon are cleaned with conc. aqua regia "pickling" for 5 hours. Then rinsed with deionized H<sub>2</sub>O for more than 10 minutes and dried with N<sub>2</sub> jet (0.1  $\mu$  filter). They are then placed in a baking furnace at about 80 °C for one hour to dry.

The Hg is weighed before loading. The excess amount of Hg is weighed again after loading. The difference weight of Hg before and after loading is the amount of Hg in crucible.

The crucible is designed such that coolant liquid could be pumped in and out so that the melt temperature is controlled. The coolant liquid temperature is controlled in a thermos reservoir and can be pumped for circulation. The cooling is accomplished by circulating the liquid through 1/4" O.D. copper coil placed in a 50-litre capacity picnic-box packed with ice. The schematic of the temperature control system of the melt crucible as shown in Fig. 6.



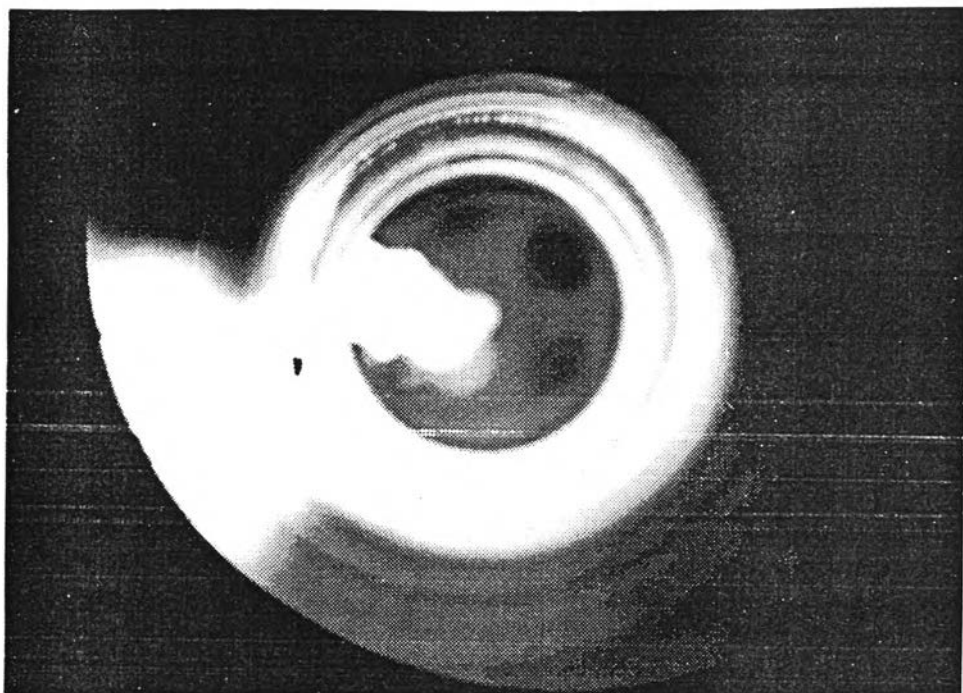


Fig.5 Surface of Hg in crucible at  $8.35^{\circ}\text{C}$   
before saturated with Sn.

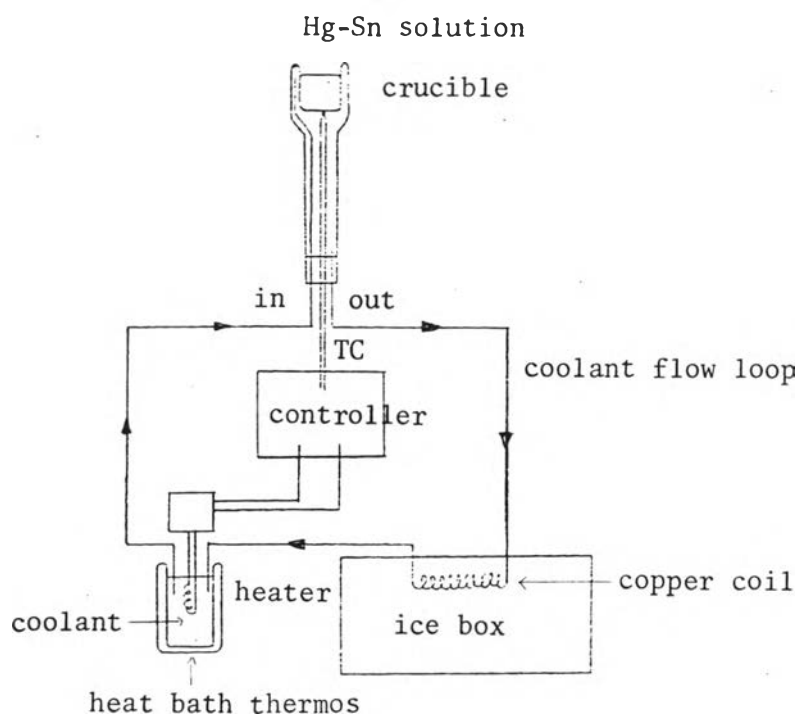


Fig.6 Schematic of temperature controlled system of the melt in crucible.

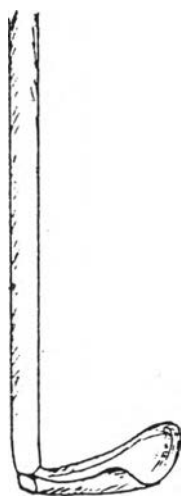


Fig.7 Saturating quartz basket.

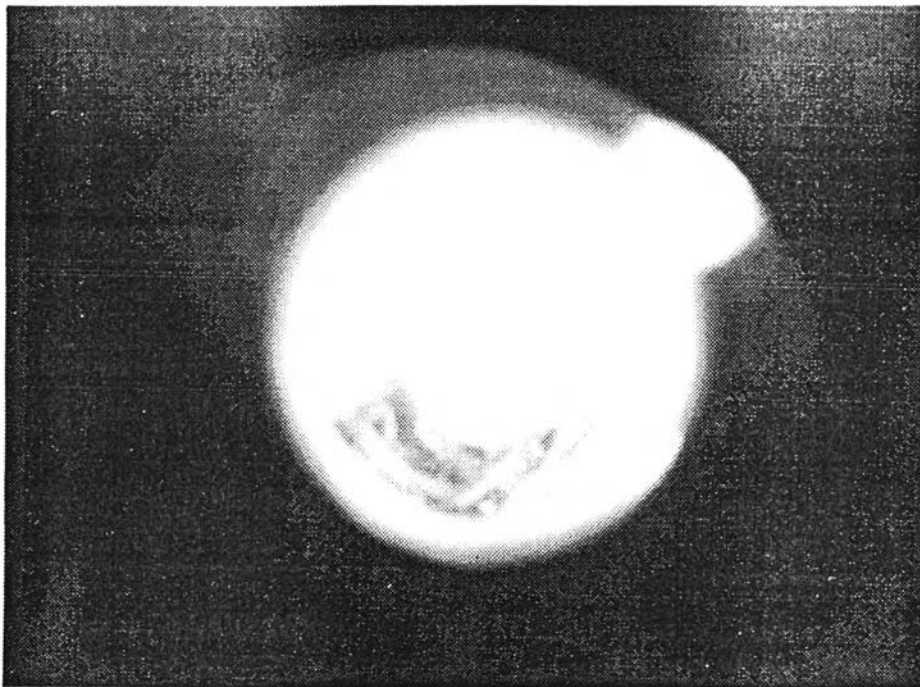


Fig.8 The melt Sn in basket during heat for cleaning approximately  $550^{\circ}\text{C}$ .

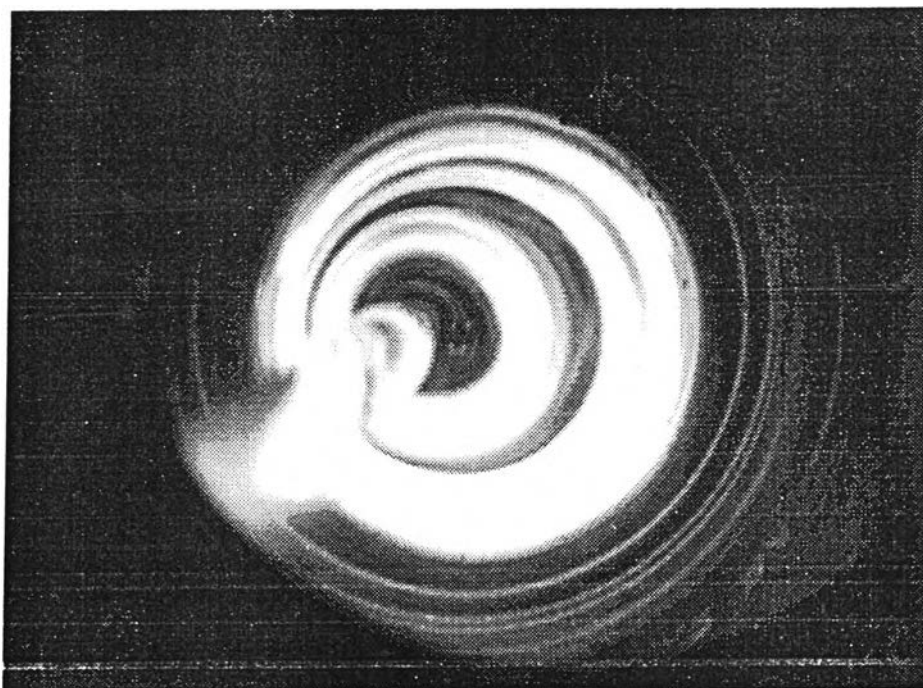


Fig.9 The surface of the melt during saturation.



The surface cleaning of the 6N purity Sn to be loaded through air-lock chamber by first etching in conc. aqua regia for 5 minutes and rinsing with deionized H<sub>2</sub>O for 10 minutes for neutralization. After that Sn is put in the quartz basket as shown in Fig. 7 and loaded in the load-lock chamber. After pumping and refilling the chamber with UPH seven times, the gate valve is opened, and the basket is lowered to the center of furnace which is maintained at about 550 °C. Sn is melted and maintained at that temperature for cleaning for about 24 hours in UPH atmosphere as shown in Fig. 8. The furnace is turned off to allow the Sn to return to room temperature. The Sn saturating basket is then moved down to saturate the Hg which is controlled at the desired saturation temperature. To promote dissolution the basket is rotated at approximately 1 rpm. The saturation is reached after approximately 20 hours as confirmed by surface partial solidification if the melt is cooled. The surface of the melt during saturation is shown in Fig. 9. Sn is weighed before loading and again after saturation. The different weight is the amount of Sn dissolved in Hg. The temperature maintained during saturation is then the saturation temperature.

#### Liquid Phase Epitaxy Procedure

Liquid phase epitaxy (LPE)(26) can be defined as the precipitation from a liquid phase of a crystalline layer onto a parent substrate such that the crystallographic orientation of the layer is determined by that of the parent substrate. LPE is simply a particular case of solution growth. Its uniqueness lies in the fact that the growth

front is determined largely by seeding. In this respect it is difficult to make a fundamental differentiation between seeded solution growth and LPE, for any such differentiation is a question of degree. Two points of difference are worthy of note. First, in solution growth seeding is usually done to provide nucleation centers at a particular location or temperature rather than to produce an essentially planar growth front. Second, seeded solution growth usually produces a comparatively large amount of "bulk" material. By comparison, LPE is usually used to grow material on a planar seed that is thin enough and planar enough to be called a "layer".

Most LPE growth systems fall into one of two classifications: a) transient systems, involving the controlled cooling of a solution in which the desired constituents have been dissolved; or b) steady-state systems, in which the system temperature is essentially constant and material is transported by the use of a thermal gradient. In illustrating these systems, it is convenient to choose a particular example. The growth of GaAs from Ga solution is chosen due to the extensive work which has been done on this system. The essential elements of the Ga-As phase diagram are shown in Fig. 10.

The more widely used method is the transient one. If a solution of composition  $X_A$  and temperature  $T_A$  (point A in Fig.10) is brought into contact with a GaAs substrate also at temperature  $T_A$ , the system equilibrium is unchanged. This is so since point A lies on the liquidus line of the phase diagram and the solution is already saturated with As. If the system is then cooled to point B, the

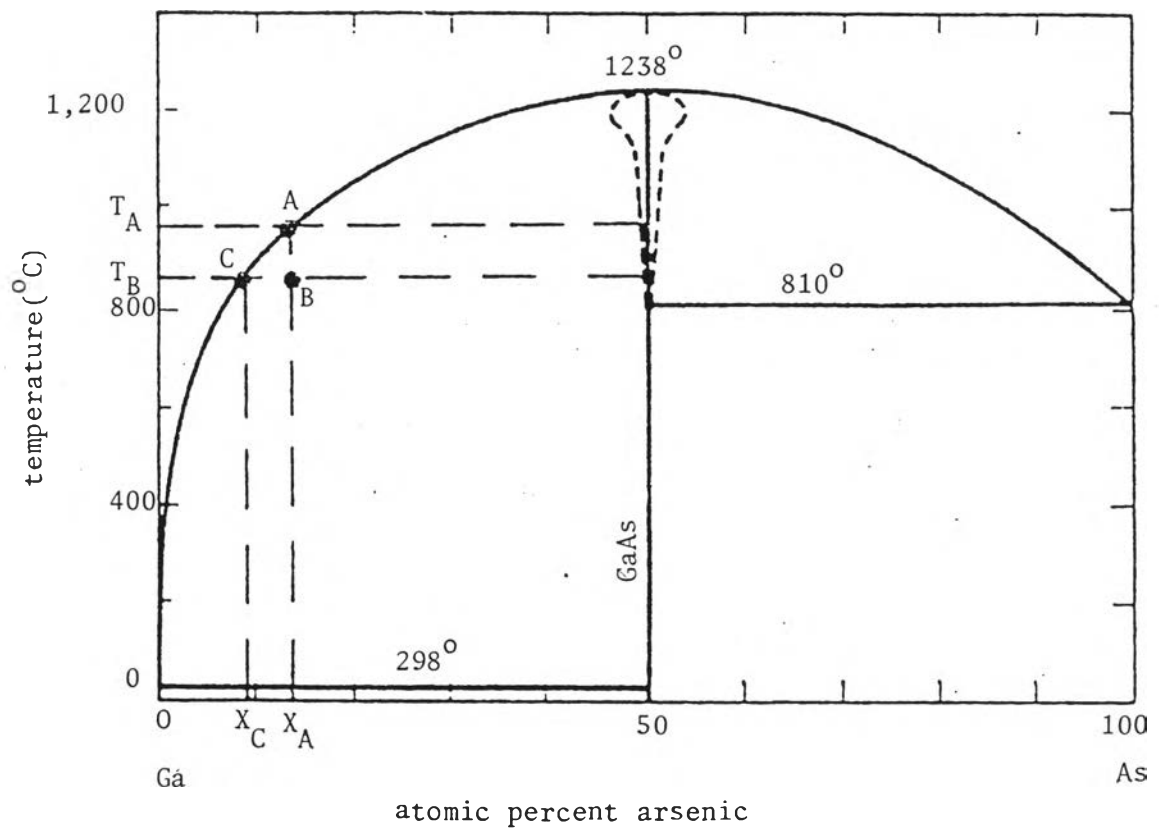


Fig.10 Ga-As phase diagram.

solution becomes supersaturated, and GaAs precipitates from the melt. Simply stated, when an As-saturated Ga solution is cooled, the decreasing solubility of As with decreasing temperature causes As to precipitate in the form of GaAs, bringing the liquid to composition  $X_c$ . Growth occurs more readily on the GaAs substrate than in the bulk of the melt and an epitaxial film is grown. The thickness of the grown film will be a function of the melt volume, the cooling range, and the area of the seed (substrate) on which growth occurs.

The second major classification of LPE growth systems is the steady-state method of growth. Consider a system in which a GaAs substrate is held at temperature  $T_B$  and a GaAs source crystal is held at a higher temperature  $T_A$ , with the space between filled by Ga. As the system approaches equilibrium, more GaAs will be dissolved at the hotter source than at the cooler substrate. Arsenic must then diffuse from the vicinity of the source to the vicinity of the substrate. A condition of supersaturation is thus created at the substrate and growth will occur.

In this section, we will discuss in detail about: 1) saturation determination  $T_s$ , phase diagram data of Hg-Sn; 2) the values of ratio  $\Delta(\text{mass of Sn out})/\Delta T_s$  as a function of  $T_s$ ; 3)  $\Delta(\text{mass})$  maximum at each  $T_s$ ; 4) growth procedure; 5) growth morphologies (optical microscope); 6) summary and discussion.

1. Saturation Determination  $T_s$  (Phase Diagram Data of Hg-Sn)

The exact saturation temperature ( $T_s$ ) determination are very important and necessary in liquid phase epitaxy procedure. The crude  $T_s$  obtained during melt saturated preparation are not enough in very thin film growth (< 1 microns). Because of the amount of solute which will solidify is too much to get very thin epitaxial film.

The method for obtaining liquidus data (saturated composition vs. temperature), the direct observation technique, can be used for accurate measurements on binary Hg-Sn system. This technique is a method for determining  $T_s$  (saturated or liquidus temperature) by heating and cooling a sample (saturated solution) of predetermined composition, rather than by finding the composition of a solution that has been saturated at a fixed temperature. The experiments are performed in VLPE system that permits the surface of the Hg-Sn solution in the crucible to be observed visually, preferably with an optical microscope through the glass window at the cover of load-lock chamber. The sample is initially heated until it becomes completely molten, at a temperature above  $T_s$ , then cooled slowly below the temperature at which solid particle (tin) formed by spontaneous crystallization first appear on the surface of the liquid as shown in Fig. 11. Because of supercooling, the temperature is generally lower than  $T_s$ . In fact the temperature can be much lower than  $T_s$ ; the cleaner the surface the lower the temperature at which crystallization can take place. In Figure 11 this takes place near  $4^\circ\text{C}$  when  $T_s$  is expected near  $10^\circ\text{C}$ . The sample is then heated, either continuously or

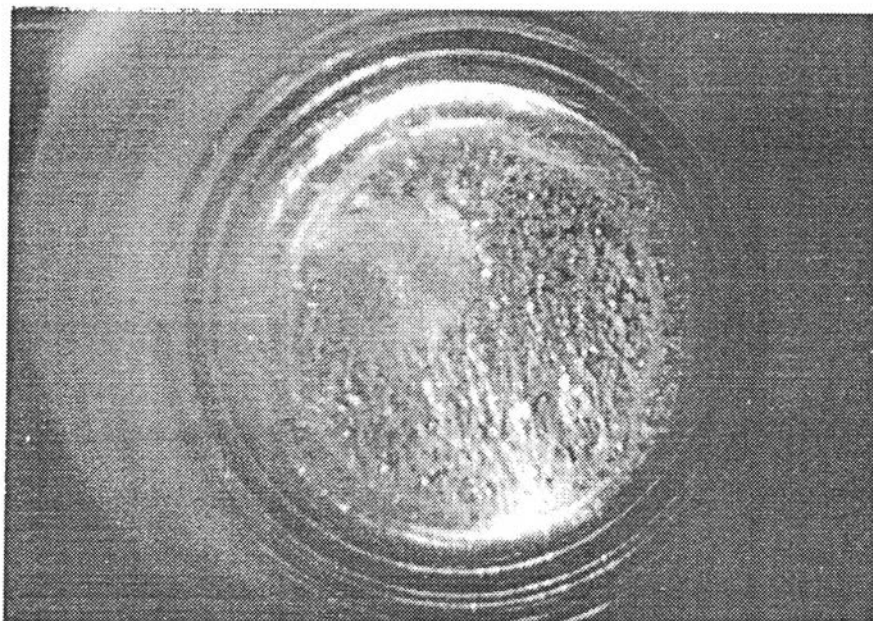


Fig.11 Sn solidification of Hg-Sn solution after the solution is cooled down  $\sim 4^{\circ}\text{C}$  from the saturated temperature  $\sim 13^{\circ}\text{C}$ .

step-wise, until the solid particles are completely redissolved, the temperature at which the last particles disappear is taken to be  $T_m$ . As with the case of super cooling, the latent heat of fusion results in apparent saturation temperature at  $T_m$ ;  $T_s$  has been over shot during the temperature rising period. The rate of temperature increase/decrease, if adequately controlled, would result in a finite solid area floating on the liquid surface, not a complete coverage as in Fig. 11 or completely liquid surface. Eventually, with small excursion of the temperature, decreasing-increasing alternately, one could gradually move the center temperature with decreasing excursion, until there exists an extremely small solid flake on the liquid surface. And as the control is exercised such that the very small flake could be controlled to increase and decrease in size at will near zero size, the equilibrium saturation temperature  $T_s$  can be approached to within a small error  $\Delta T$ . It is applicable only to systems in which the solid phase is less dense than the liquid phase. Fig.12 show phase diagram of Hg-Sn as determined by this work compare with the other works.(27) The full-line liquidus is that of gray tin (stable) and the dashed line that of Hg Sn<sub>12</sub> ( $\gamma$ ) (metastable). This work was plotted by (+) symbol indicating much higher  $T_s$  than the published values. This is because we use only one decrease/increase temperature excursion cycle and hence the higher apparent  $T_s$  (i.e. the  $T_m$  discussed earlier). Because our temperature control is not adequate in the dynamic mode, and because the thermal mass of the melt is so large that equilibrium could not be reached within practical time, we were forced to abandon our effort to independently establish the phase diagram in this range

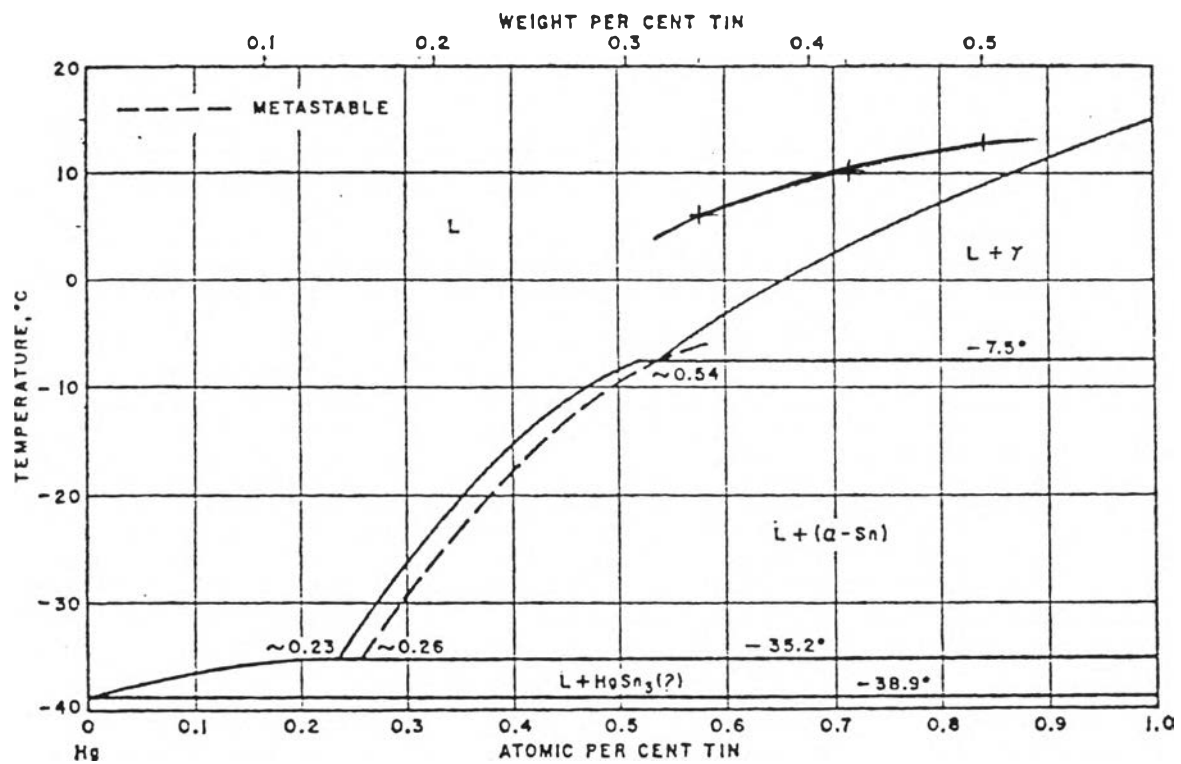


Fig.12 Phase diagram of Hg-Sn.



of solubility. Adopting the published result of Fig. 12, the errors in our results are in the right direction and have the right trend as a function of the temperature.

## 2. Estimate of $\Delta(\text{Mass of Sn Out})/\Delta T_s$ as a Function of $T_s$

Using the published phase diagram of Hg-Sn in Fig. 12, we can calculate the value of  $\Delta(\text{mass of Sn out})/\Delta T_s$  as a function of  $T_s$  : .013, .015, .017 wt%/ °C at saturated temperature 6°, 10°, 13° C respectively. In liquid phase epitaxial growth of  $\alpha$ -Sn on InSb we must grow the layer thickness < 1 micron. From reference (12)  $\alpha$ -Sn becomes unstable beyond 1 micron thickness. To afford better thickness control one should use large volume melt crucible, large area substrate, and very small  $\Delta(\text{mass of Sn out})/\Delta T_s$  value. Our system, however cannot be temperature-controlled to sufficient accuracy.

## 3. Estimate of $\Delta(\text{Mass})$ Maximum at Each $T_s$

The crucible in our system can contain the Hg-Sn solution to approximately 500 gm. The lowest saturation temperature  $T_s$  which could be maintained is about 4 °C. We can supercool the Hg-Sn solution by an amount  $\Delta T_0$  ;  $\Delta T_0 \approx 2, 6, 9$  °C at  $T_s \approx 6, 10, 13$  °C by respectively. Therefore the  $\Delta(\text{mass})$  maximum at each  $T_s$  are 130, 450, 765 mg at  $T_s \approx 6, 10, 13$  °C respectively by theoretically.

#### 4. Growth Procedure.

The dipping procedure uses a vertical growth tube, with a crucible containing the solution Hg-Sn at the lower end of the tube and the substrate InSb fixed on a moveable holder. Epitaxial growth is initialized the holder to immerse the substrate in the solution, and contact is terminated by raising the holder to its original position. In our experiment, we heat the substrate at approximately 475 °C for 45 minutes to desorb passivating oxide layer before starting an appropriate dipping procedure. The growth parameters are saturated temperature, dipping temperature, cooling rate, minimum temperature, degrees of supercooled temperature, etc.

While  $T_s$  determines the solubility limit of Sn in Hg, it does not determine the solubility of InSb, if any, in Hg. If indeed InSb is soluble in Hg one would also expect different rates of dissolution for the {111}A and {111}B faces of the substrate. Thus the initial moment after the InSb substrate is immersed in the liquid at a temperature near the  $T_s$  (of Sn in Hg), depending on the rate, if any, of Sn deposition on to the InSb substrate in comparison with the substrate dissolution into Hg, the net result can either be etching (loss of substrate material) or growth (of Sn on the substrate).

The epitaxy experiments can be roughly grouped into 4 "methods" :-

1) The melt is maintained at a constant temperature by an amount  $T$  below  $T_s$ , i.e. supercooled, before and after sample

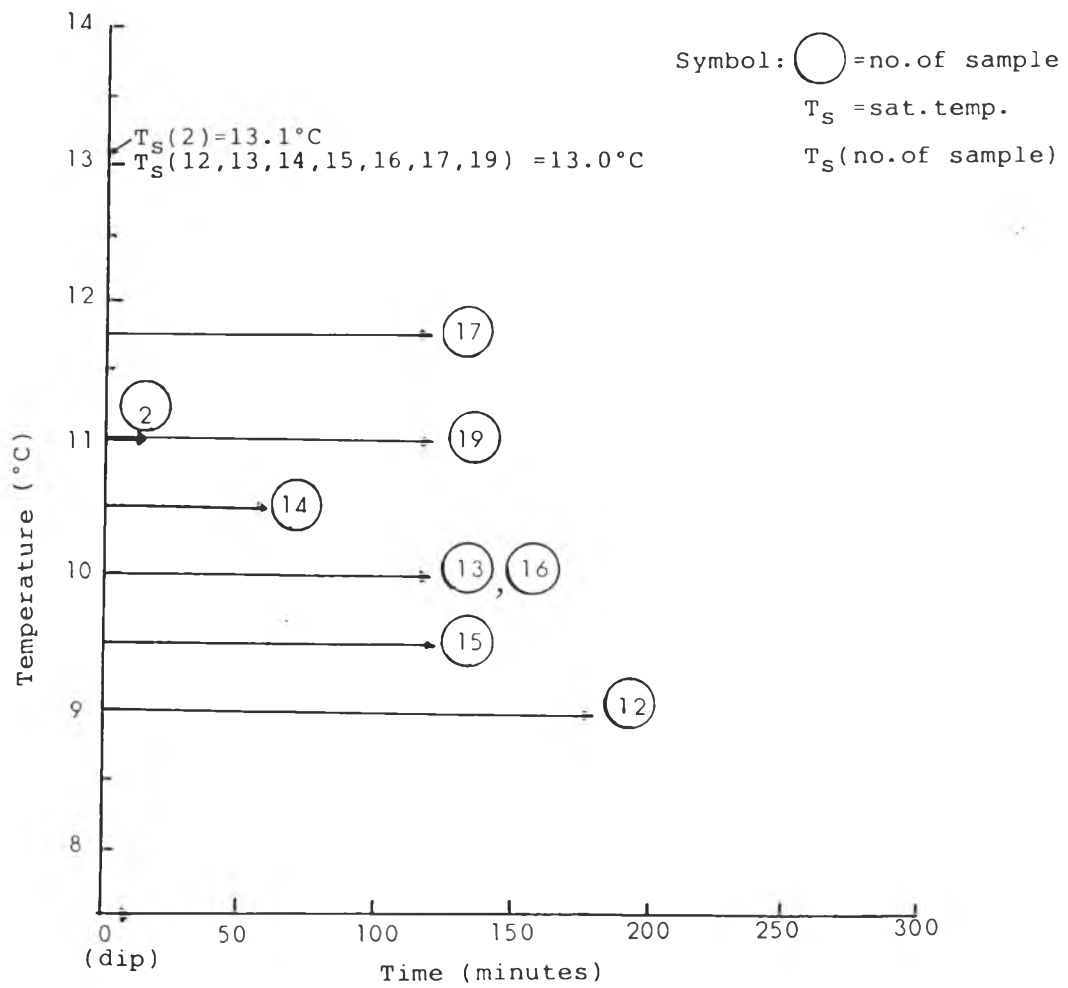


Fig.13 The temperature program of the method 1) which is super-cooled before dipping and maintaining constant temperature.

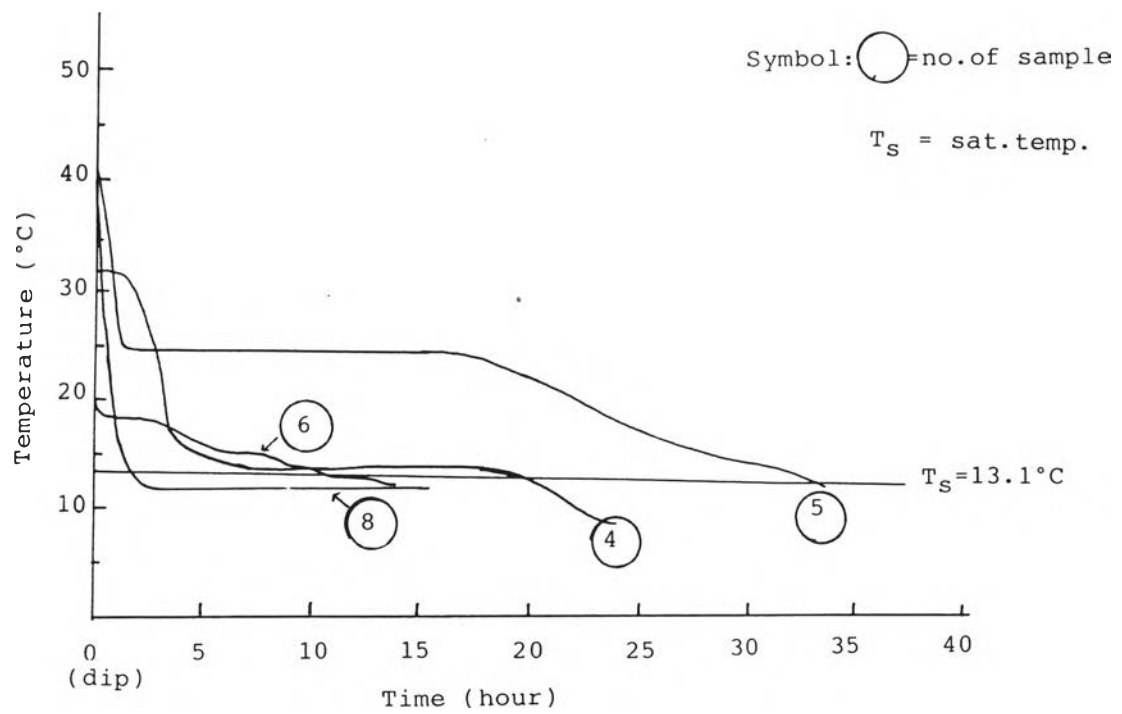


Fig.14 The temperature program of the method 2) which is dipping at high temperature(20-40°C) then decrease temperature until  $T < T_s$  and maintaining constant temperature.

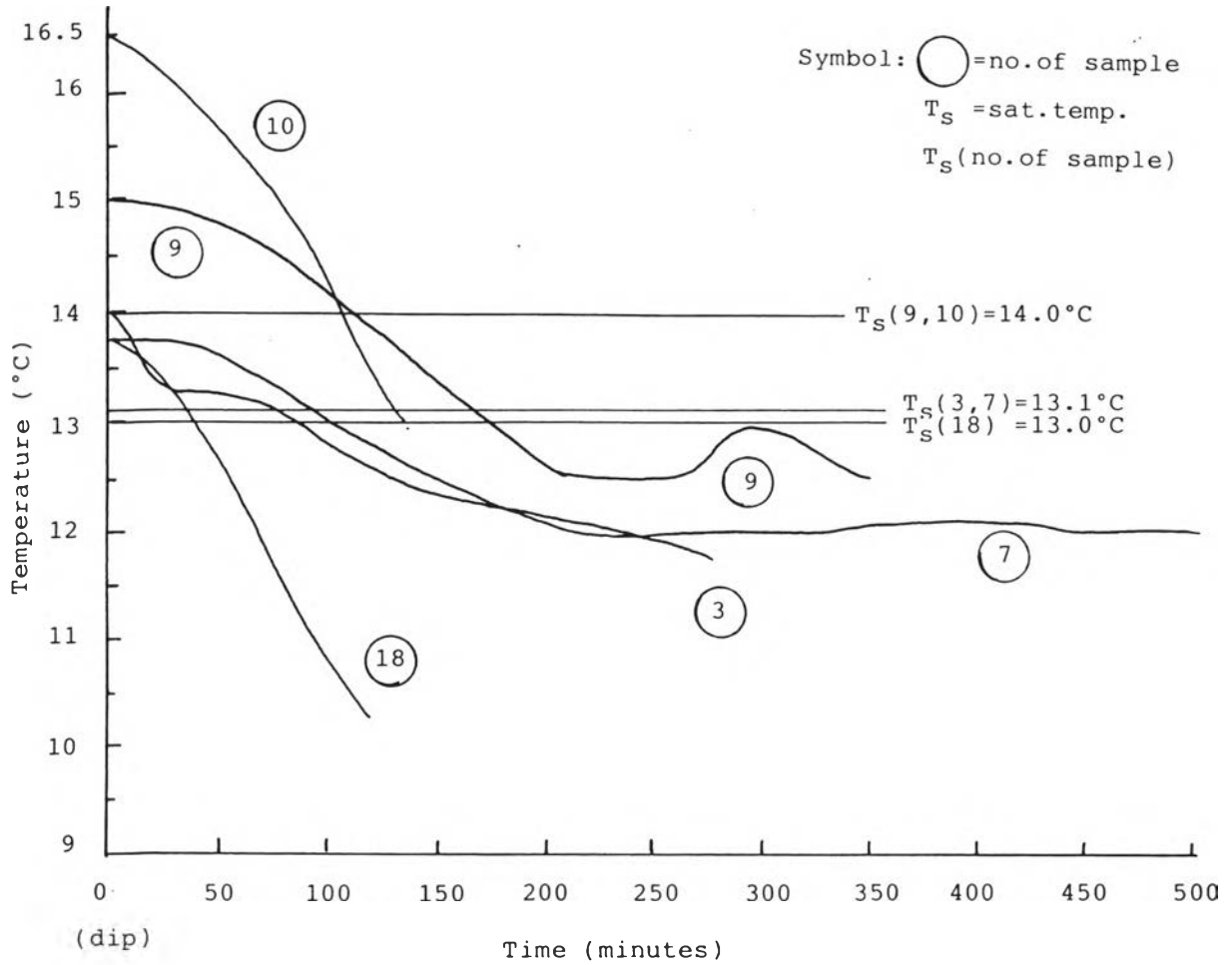


Fig.15 The temperature program of the method 3) which is dipping at low temperature 14-16°C but  $T > T_s$ , then decrease temperature.

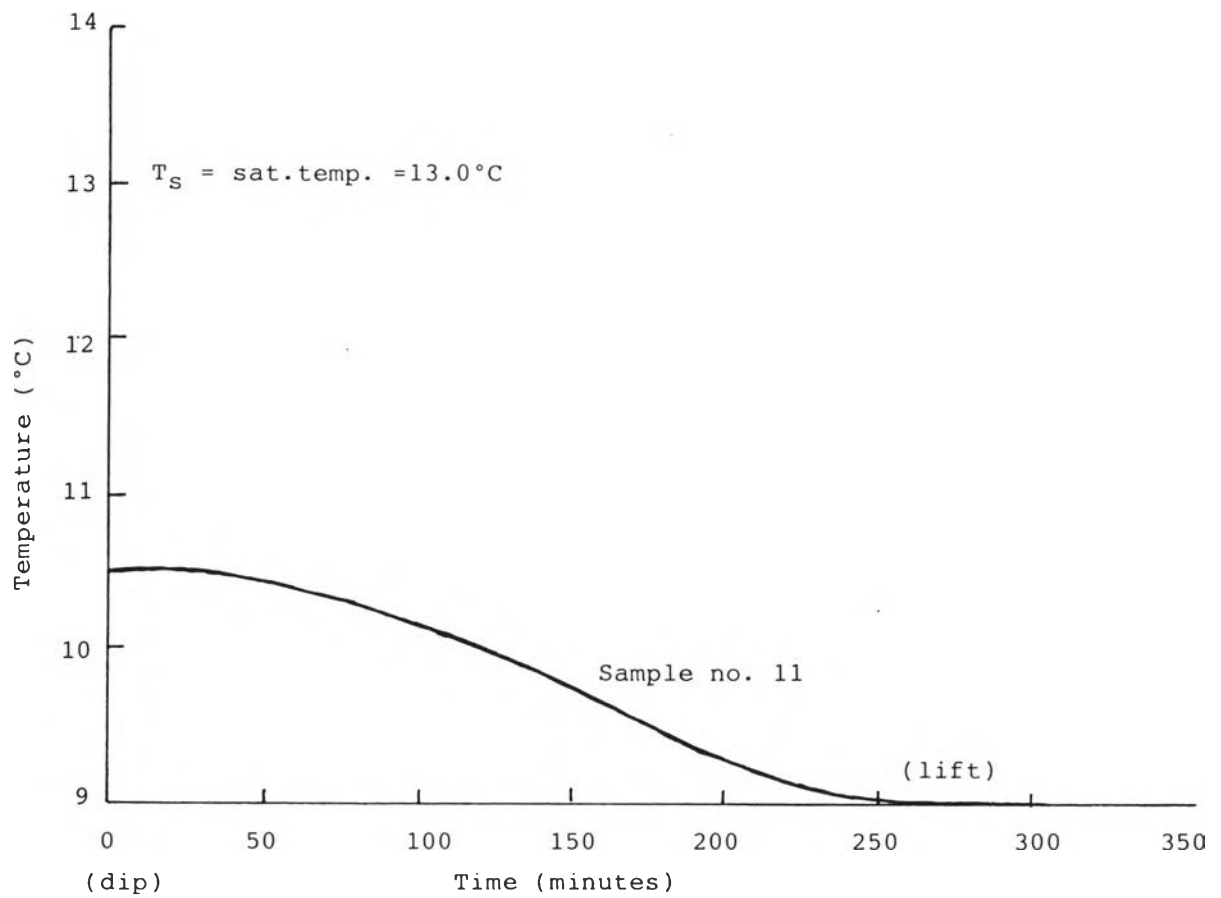


Fig.16 The temperature program of method 4)  
which is dipping after decrease  $T < T_s$ , then  
decrease temperature.

Table 2 LPE parameters of all samples in this study.

Dipping no.	Date	Saturation Temperature	Dip Condition	Dip Temperature	Minimum Temperature	Dip Time	Increasing Weight of Sample
1	4 JAN 1985	12-13 C	Steady-State	7.5 C	7.5 C	10 min.	-
2	31 AUG 1985	13.1 C	Steady-state	11.0 C	11.0 C	15 min.	5.9 mg.
3	30 SEP 1985	13.1 C	Transient	14.0 C	11.75 C	4 hr., 43 min.	- 3.5 mg.
4	6 OCT 1985	13.1 C	Transient	31.2 C	8.5 C	24 hr.	90.2 mg.
5	11-13 OCT 1985	13.1 C	Transient	41.0 C	12 C	44 hr., 45 min.	75.8 mg.
6	17-18 OCT 1985	13.1 C	Transient	21.0 C	12.25 C	14 hr.	10.5 mg.
7	21 OCT 1985	13.1 C	Transient	13.75 C	12.00 C	8 hr., 30 min.	5 mg.
8	23-24 OCT 1985	13.1 C	Transient	40.0 C	12.00 C	15 hr., 40 min.	14 mg.
9	25 MAY 1985	14.0 C	Transient	15.0 C	12.50 C	6 hr., 10 min.	1.2 mg.
10	29 MAY 1986	14.0 C	Transient	16.5 C	13.0 C	2 hr., 15 min.	3.1 mg.
11	24 AUG 1986	13.0 C	Transient	10.5 C	9.0 C	5 hr., 5 min.	4.9 mg.
12	26 AUG 1986	13.0 C	Steady-State	9.0 C	9.0 C	3 hr.	2.8 mg.

Dipping no.	Date	Saturation Temperature	Dip Condition	Dip Temperature	Minimum Temperature	Dip Time	Increasing Weight of Sample
13	20 MAR 1987	13.0 C	Steady-State	10.0 C	10.0 C	2 hr.	4.6 mg.
14	24 MAR 1987	13.0 C	Steady-State	10.5 C	10.5 C	1 hr.	4.9 mg.
15	27 MAR 1987	13.0 C	Steady-State	9.5 C	9.5 C	2 hr.	0.7 mg.
16	4 APR 1987	13.0 C	Steady-State	10.0 C	10.0 C	2 hr.	3.6 mg.
17	5 APR 1987	13.0 C	Steady-State	11.75 C	11.75 C	2 hr.	1.4 mg.
18	6 APR 1987	13.0 C	Transient	13.75 C	10.25 C	2 hr.	-
19	8 APR 1987	13.0 C	Steady-State	11.0 C	11.0 C	2 hr.	-

- Remarks
1. Dipping no.3, weight of sample decreased
  2. Dipping no.15, rotate the substrate 2 rounds after dipping for 30 min.
  3. dipping no.16, rotate the substrate all time after dipping for 30 min.
  4. Dipping no.18 and 19, no crystallization



immersion. In Fig. 13 the temperature and the time duration for each and several runs are shown and  $T_s$  indicated.

2) The sample is dipped into the melt originally at  $T \gg T_s$ . The surface of the substrate is etched at an appreciable rate depending on the excess of  $T$  over  $T_s$ . The temperature is then decreased to below  $T_s$ . See the temperature programs in Fig 14.

3) The sample is dipped into the melt originally at  $T$  only slight above  $T_s$ . The Sn depositon rate is higher and the substrate etch rate is lower than the corresponding rates in method 2). See the temperature programs in Fig. 15. Note the various temperature change rates.

4) The sample is dipped into the melt originally at  $T < T_s$ , then temperature is decreased further. The substrate surface is etched very slowly and the rate of deposition is very low too. The temperature program of sample no. 11 is shown in Fig. 16.

Table 2 summarizes for record purpose the experimental conditions of all epitaxy experiments in this work.

##### 5. Growth Morphologies (Optical Microscope).(28)

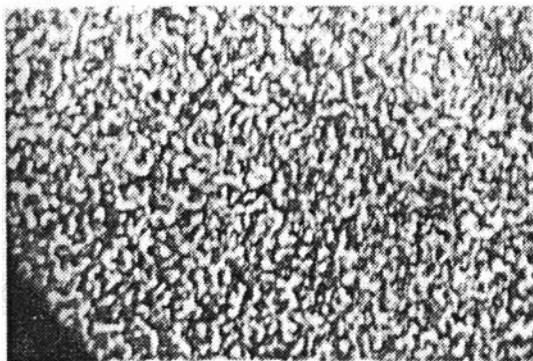
The basis of the investigation of the as-grown crystal surfaces lies in the following facts: the crystals grow or dissolve always through the surface, and the macro-morphology of a crystal is the total sum of its surfaces. The surface micro-morphology is

subjected to two factors; i.e., intrinsic and extrinsic factors. The intrinsic factors may be the crystal structure, the surface symmetry, and the constituent atoms which are inherent in a crystal. The extrinsic factors are such external conditions as supersaturation, concentration, temperature, pressure, imperfections and impurities in the surroundings.

It is generally believed that the optical methods are so severely limited in resolution that they are unsuitable for the observation of the atomistic features. This is true as far as the lateral resolution is concerned, and the best lateral resolution is  $\lambda/2$  ( $\lambda$  = the wavelength of the light). But if we do not confine ourselves to the resolution in the strict sense of the word, there are several other optical means by which we can detect a small step height of less than  $\lambda/2$ . For instance, dark-field illumination creates a bright contrast at the step edges by the scattered light against the dark background, and this can reveal a step height which is less than  $\lambda/10$ . This method is used in studying crystal surface of all our samples. A magnification of about 200 is used to study the crystal growth mechanism as indicated by the surface morphology.

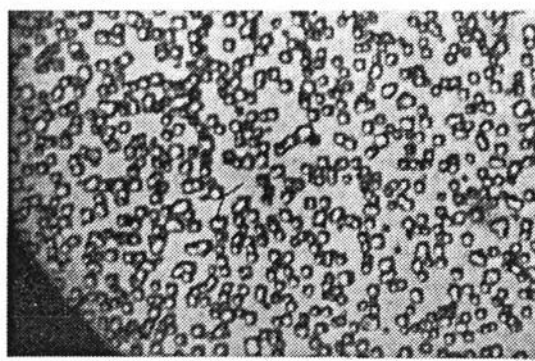
The growth morphologies of the surface after growth via "method 1" (constant, supercooled temperature) are shown in Fig. 17, for {111} substrate, at various supercooled temperatures and for various durations. For a small  $T$  in Fig. 17 a, ( $T = 10.5^\circ \text{C}$ ) the surface shows irregular pattern of etching. Deposition of Sn, if any, has to follow the surface contour. Etch rate  $>$  deposition rate. In Fig. 17 b, ( $T = 10^\circ \text{C}$ ) the etch rate is slower. Evidently the Sn

(a)  $\Delta T_0 = 2.5^\circ\text{C}$ ,  $t = 1\text{hr.}$ ,  $T = 10.5^\circ\text{C}$



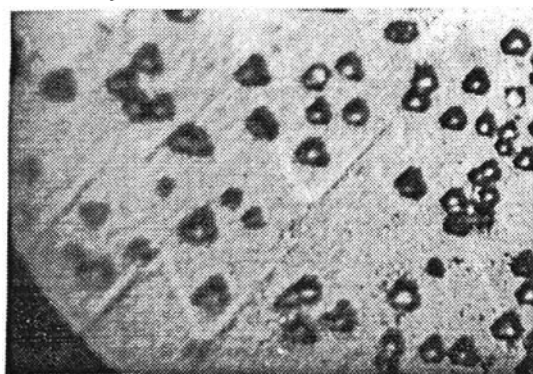
sample no.14

(b)  $\Delta T_0 = 3.0^\circ\text{C}$ ,  $t = 2\text{hr.}$ ,  $T = 10.0^\circ\text{C}$



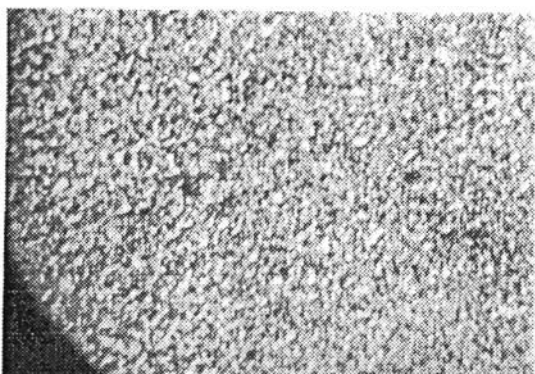
sample no.13

(c)  $\Delta T_0 = 3.0^\circ\text{C}$ ,  $t = 2\text{hr.}$ ,  $T = 10.0^\circ\text{C}$



sample no.16

(d)  $\Delta T_0 = 3.5^\circ\text{C}$ ,  $t = 2\text{hr.}$ ,  $T = 9.5^\circ\text{C}$



sample no.15

(e)  $\Delta T_0 = 4.0^\circ\text{C}$ ,  $t = 3\text{hr.}$ ,  $T = 10.0^\circ\text{C}$



sample no.12

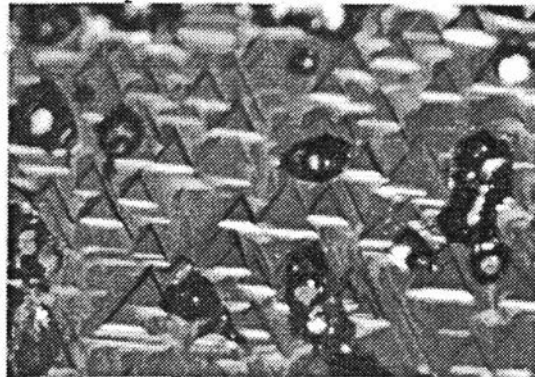
Fig.17 Optical micrographs in dipping method 1) which showed the islet form of tin ( $\alpha$  or  $\beta$ ) of different site distribution density. Magnification 200X.

deposition rate is not uniform and Sn islets are formed on random nucleation sites. In other case shown in Fig. 17 c, under the same conditions a different substrate shows lower density of nucleation sites each supporting larger islet growth than that in Fig. 17 b. Also in Fig. 17 c the islets show crystal facets that are aligned, i.e.; these islets are epitaxial on the substrate. In Fig. 17 d relatively little etching is observed and the growth islets are very small. In Fig. 17e etching is observed only in some area, but in which no islet growth is observed. There may be a thin film of Sn on the areas perceived as having been etched slightly.

The growth morphologies of the surface growth via "method 2" (sample immersed at  $T$  much higher than  $T_s$ ) exhibit much coarser etched patterns. Fig. 18 shows etch-growth patterns corresponding to the temperature programs shown in Fig. 14. This group of substrates, however, is of  $\{111\}A$  orientation. Triangular etch facets are exposed. The size and sharpness of the etch facets are temperature and time dependent, as to be expected. In Fig. 18 a-d there are no visible evidence of Sn growth. The Figures 18a and 18b reflect the effect of etching time while the pair 18 c, 18 d reflects the effect of the initial temperatures. It is difficult to perform more systematic studies of the etch time and/or temperature in that the etching cannot be studied on the same substrate.

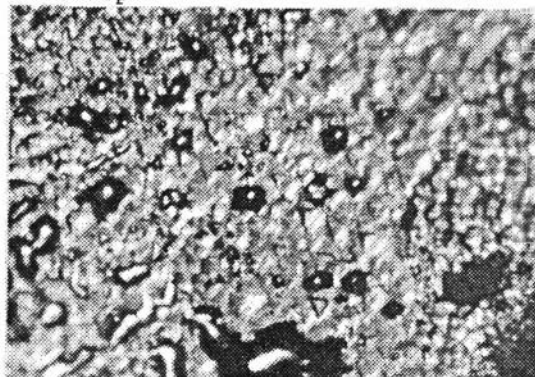
The surface morphologies of the samples that underwent "method 3" experiments, i.e. immersed at a temperature only slightly above  $T_s$  and allowed to collect Sn on the surface at  $T < T_s$  per

(a)  $T_{\text{dip}}=41^{\circ}\text{C}, t=44\text{hr.}, 45\text{min.}$



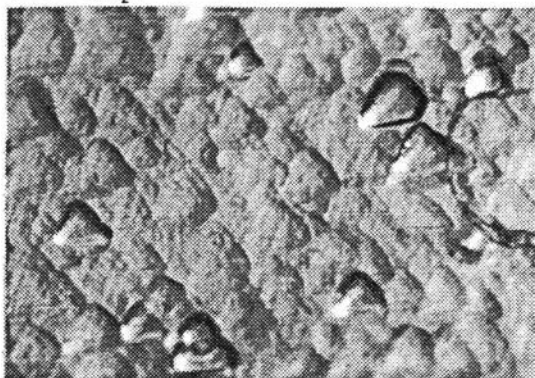
sample no.5

(b)  $T_{\text{dip}}=40^{\circ}\text{C}, t=15\text{hr.}, 40\text{min.}$



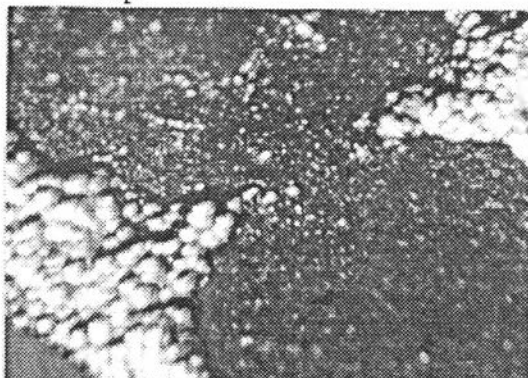
sample no.8

(c)  $T_{\text{dip}}=31.2^{\circ}\text{C}, t=24\text{hr.}$



sample no.4

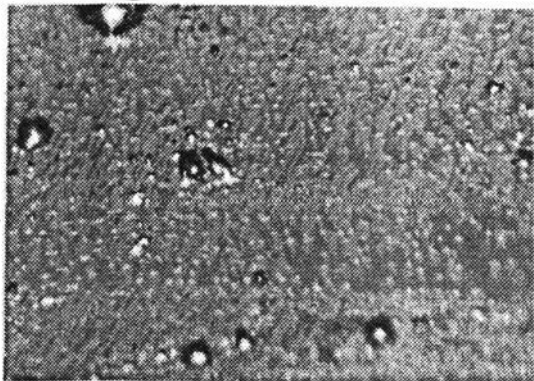
(d)  $T_{\text{dip}}=21^{\circ}\text{C}, t=14\text{hr.}$



sample no.6

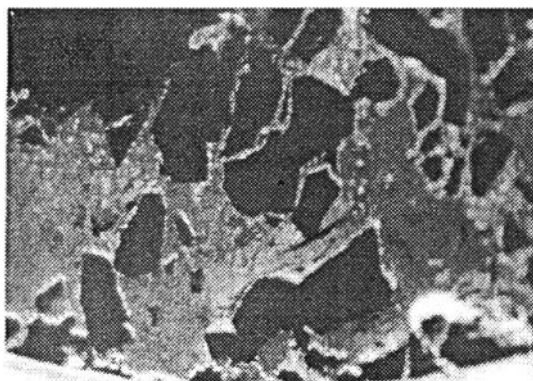
Fig.18 Optical micrographs in dipping method 2) which showed the etch patterns in triangular form as a result of dipping at high temperature 20-40°C. Magnification 300X.

(a)  $T_{\text{dip}}=14.0^{\circ}\text{C}$ ,  $t=4\text{hr.}, 43\text{min.}$



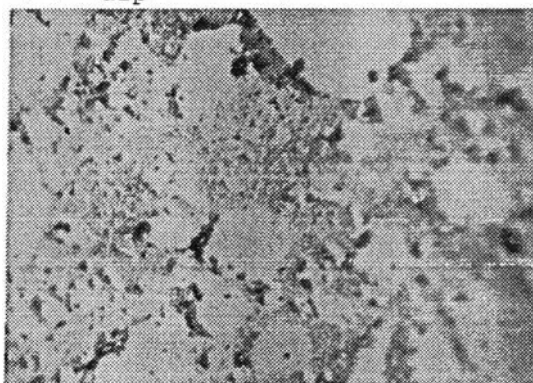
sample no.3

(b)  $T_{\text{dip}}=15.0^{\circ}\text{C}$ ,  $t=6\text{hr.}, 10\text{min.}$



sample no.9

(c)  $T_{\text{dip}}=13.75^{\circ}\text{C}$ ,  $t=8\text{hr.}, 30\text{min.}$



sample no.7

Fig.19 Optical micrographs in dipping method 3) which showed the texture of a heavy deposit of Sn in the form of randomly shaped islets in (a), Fig.(b) showed thin foil covered the surface of InSb, Fig(c) showed thin foil covered the surface of InSb.

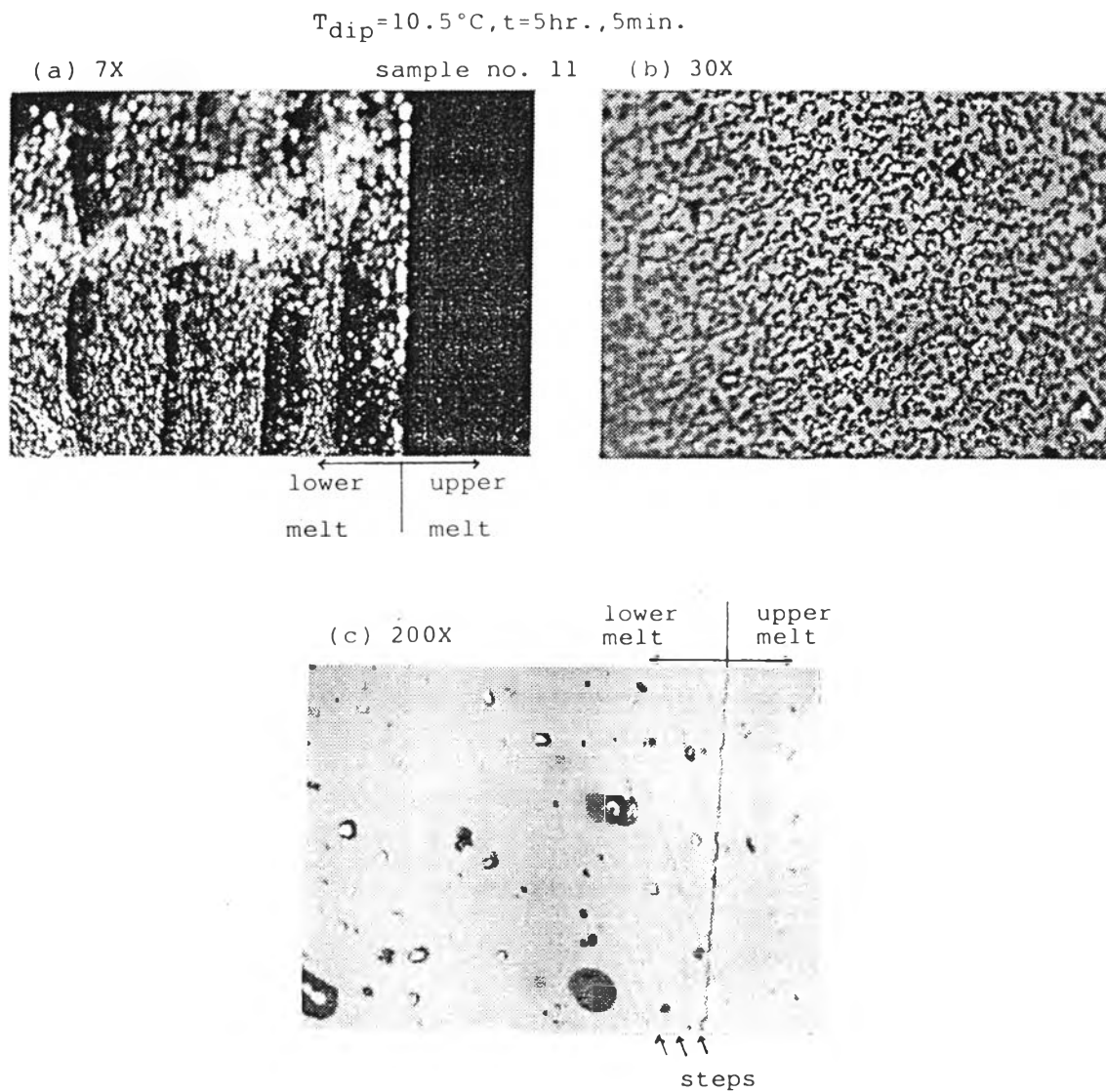


Fig .20 Optical micrographs in dipping method 4) which showed surface morphology at different magnifications 7X, 30X, 200X in (a), (b), (c) respectively. Fig.(a) showed general characteristic of surface. Fig.(b) showed the islet form of crystals. Fig.(c) showed the area is very smooth having the steps in the same direction. Using EPMA/WDS in the next chapter showed that it is Sn-thin film.

temperature-time profiles shown in Fig. 15, are shown for samples 3, 7 and 9 in Fig. 19 a, b and c respectively. Generally the results are poor. Sample 3 in Fig. 19 a shows the texture of a heavy deposit of Sn in the form of randomly shaped islets. But the deposit is only on patches of area and Fig. 19 a merely investigates an area with such deposit. In Fig. 19 b, with longer growth time, shows a region where the tin deposit has coalesced into continuous tin foil. Subsequent investigation using the scanning electron microscope shows that this foil growth too starts from discrete nucleation site underneath. In Fig. 19 c shows deposit similar to that in Fig. 19 a except now the "surface grain size" is large.

The surface morphology of sample 11, which underwent "method 4" experiment with the temperature profile shown in Fig. 16, is shown in Fig. 20 for areas near the partial dipping boundary. Islet growth of varied site density is seen. In Fig. 20 c smooth surface with aligned steps is seen, and as described in the next chapter, is shown to be thin film of Sn.

## 6. Summary

From visual inspection using a microscope with magnifications up to 300X the following remarks can be made. There exists an etching action of the InSb substrate by the Hg-Sn melt. High temperature etching (40-50 °C) results in rough surface morphology; the etch pits are deep. The etched surface is less rough at lower etch temperatures. Therefore it appears advisable to start with a melt of low concentration of Sn in Hg, so that  $T_s$  is low. One



then may immerse the sample at the low  $T > T_s$ ; both are low temperatures, perhaps  $6^\circ \text{C}$ . This would promote etching at a slow rate while (since  $T > T_s$ ) there would be no deposition of Sn. Once the surface is etched in sites (in the Hg-Sn) then the temperature can be set lower than  $T_s$  to obtain thin film Sn growth. At these low temperatures all rates of action would be slow and good thin -Sn film may be obtained.

Unfortunately our temperature control system could not work well below  $8^\circ \text{C}$ , and the time required for such experiment would be prohibitive. Our experiment were done over tens of hours at the higher temperatures; lower action rate would take tens of days. It is unlikely that the system cleanliness can be maintained; there was appreciable loss of surface brightness of the melt indicative of some contamination when the melt has to be maintained at a low temperature for very long time. In fact, some of the surface morphologies observed were due to the slag attached to the sample when the latter was pulled off the melt at the end of the run.

Thus much of the useable results are those from the more fortunate cases when the epitaxy system was clean before use, the loading of the sample suffers no accident (letting in air), moving of the sample holder rod does not break the O-ring seal, etc. With luck the experimental parameter  $T$  is meaningful, else other causes such as slag would overshadow the relevant parameter. Experimental results reported are of necessary selected; much of the obviously bad results due to other causes are discarded.

With the above caveat we concluded that the results obtained with lower immersion temperature and Sn deposition at lower temperature would have the best chance of growing epitaxial  $\alpha$ -Sn on InSb.