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Relation of Heat Transfer with the Growth Rate of InSb based Bulk Crystals Grown by VDS and its Effect on the Crystal Quality

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Vertical Directional Solidification (VDS) is a crystal growth technique used to grow the bulk crystals of semiconductor materials by solidification of the melt in the vertical direction. In the growth process, the constituent elements are filled in the quartz ampoule and temperature of the ampoule is raised to a temperature well above the melting point of the constituent elements to obtain the melt. Then the melt is solidified by cooling in the vertical direction from the bottom of the ampoule. Thus it becomes a thermodynamic process where the heat is exchanged between the melt and the surrounding, and the cooling rate depends on the temperature gradient at the solid-melt interface. In the VDS system the temperature gradient can be controlled between 12 °C/cm to 24 °C/cm. Estimation of heat exchange during the growth process, using the concept of enthalpy indicate that, for the crystal growth of InSb by VDS technique, the growth rate must be less than 9 mm/hour when the temperature gradient is 20 °C/cm. Indium antimonide (InSb) is a narrow-band gap semiconductor material obtained from the elements of III-V groups indium (In) and antimony (Sb). Among all the III-V binary semiconductors InSb is the most studied semiconductor because of its narrow energy band gap (0.17 eV). Considering importance of bulk semiconductors, InSb based crystals (ingots) were grown by VDS technique at different temperature gradients in the range of 12 °C/cm to 24 °C/cm. The grown ingots were sliced to ~ 500 μm thick wafers for the characterization. Results show that the crystals grown at low growth rate (~ 3 mm/hr) are good quality single crystals with maximum mobility up to 44500 $cm^2/V{\cdot}s$ at room temperature (300 °C).

Keywords: Heat transfer, Growth rate, Melt-Solid interface, Detachment, Temperature gradient.

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1. INTRODUCTION

Bulk crystals of semiconductor materials are the pillars of modern semiconductor technology. Especially use of semiconductor crystals in optoelectronics or fiber optic communications has become most important in the semiconductor technology. Also, tailoring of crystal properties plays a crucial role in crystal growth technology and the related science because in the semiconductor technology, such properties are responsible for the revolution of electronic industries and consequently for the benefit of our society. Day by day a demand of the devices that are operating in mid-infrared (MIR) region of the electromagnetic spectrum is increasing. These devices are significant in the instrumentation used for the protection of environment, medical diagnostics and therapy, precise control of the industrial process, free-space communication etc. [1-3]. Semiconductor materials with narrow energy band-gap derived from the compounds of III-V group of the periodic table are of great interest from the infrared optoelectronics viewpoint [4]. Among all the III-V binary semiconductors, indium antimonide (InSb) is the most studied semiconductor because of its smallest energy gap (0.17 eV) and its robust properties. However these properties of the semiconductor materials which decide quality of the crystal, mainly depends on the source materials purity, crystal growth technique and the growth parameters. Vertical Directional Solidification (VDS) technique is a crystal growth technique that has easy control on the growth parameters and thus on the crystal quality. In VDS technique, the crystal is grown by solidification of the melt in vertical direction which involves heat exchange between the melt and the surrounding. The VDS technique has proved its excellence in the production of homogenous, uniform and good quality single crystal due the precise control on the translation rate and temperature gradient required for the effective heat transfers [5-6].

The growth of an ingot of bulk single crystalline materials remains one of the most challenging and astonishing technical endeavors of synthesis of materials. Along with the basic problems related to solid-state thermodynamics and kinetics, the process of crystal growth is closely linked with various physical phenomena. These phenomena include the transport of heat and mass, momentum of the elements, heat radiation from the grown crystal, transitions in the phase, effect of capillarity, and anisotropy of physical properties. Understanding of these phenomena and their connection with the growth parameters and related characteristics of the crystal, become very important and essential study for the growth of high-quality (i.e., the ones with low defect density and good uniformity) bulk crystals [7].

2. THEORETICAL BACKGROUND

Since the growth of a crystal from melt by solidification is a thermodynamic process, it becomes necessity to consider the thermal interaction between the melt and the solid at the interface. During the crystal

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growth process, there exist both the phases (solid and liquid) of the material in the ampoule. The co-existence of the two phases is well described by Gibb's Free Energy (G), introduced by the thermodynamics equation:

$$\Delta S = -\frac{\Delta G}{\Delta T}, \quad (1)$$

where S is the entropy of the total system at temperature T. As per the theory of thermodynamics, entropy always increases (or maximum at equilibrium) and the Gibbs Free energy is always minimum. This indicate that, every thermodynamic process will attempt to minimize the Gibbs free energy. Application of this concept to the solidification process suggests that, the state of single-crystalline structure will be a normal state when the potential G is minimum which is possible if the atoms and molecules i.e. 'crystal growth units' are perfectly packed in a three-dimensional crystal lattice, i.e. the atomic bonds are saturated regularly.

The basic equation of the thermodynamic potential of Gibbs is:

$$G = H - TS, \quad (2)$$

where H is the Enthalpy of the thermodynamic process.

To use the concept of Gibbs free energy for the process of crystal growth, we can consider solid phase and liquid phase (melt) as two interacting systems with Gibbs free energies G_1 and G_2 as shown in the Fig. 1.

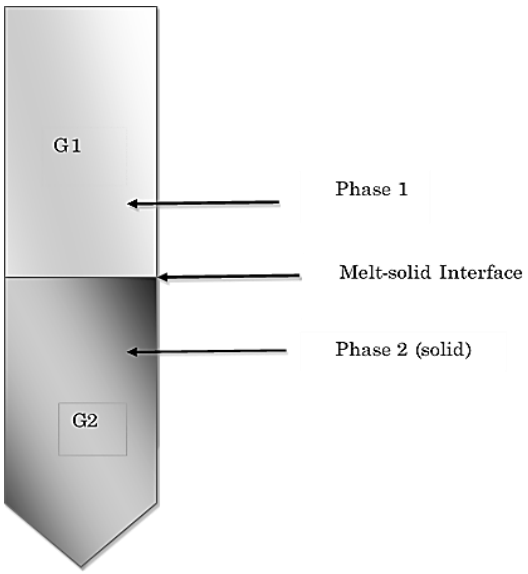


Fig. 1 – Two phases of the material and melt-solid interface

The crystal growth is characterized by a phenomenon of first order phase transition which involves two phases in contact (phases 1 and 2) separated by an interface which is treated as the melt-solid interface and the growth is carried out by maintaining a condition near equilibrium. The Gibbs potentials of the two phases (G_1 and G_2) attain equal values when the phases are in equilibrium and the potential difference is zero (i.e. $\Delta G = 0$). Hence at uniform temperature and pressure, the equation (2) for phase 1 and phase 2 becomes:

$$\Delta G = \Delta H - T\Delta S = 0. \quad (3)$$

Here ΔH is the enthalpy, which must be released during the crystallization process (latent heat of fusion), ΔS is the transition (melting) entropy and T is the temperature of the equilibrium state (melting point). Thus, there is abrupt change in the entropy, enthalpy, volume and internal energy at the phase transition. Therefore equation (3) becomes:

$$\Delta H = T\Delta S \quad (4)$$

This is of practical significance for the crystal growth. For example, the liberated heat which is related to the growth-rate participates in the thermal balance at the interface during melt-solid phase transition according to an equation [8]:

$$k_1 \frac{dT_l}{dz} - k_2 \frac{dT_s}{dz} = \frac{\Delta H}{C}\upsilon \quad (5)$$

or

$$k_{l,s} \frac{dT_{l,s}}{dz} = \frac{\Delta H}{C}\upsilon, \quad (6)$$

where $k_{l,s}$ is the thermal diffusivity, $dT_{l,s}/dz$ is the temperature gradient along the growth axis z in the liquid (l) and solid (s) phase, C is the heat capacity and υ is the growth rate.

Since the crystal growth is a thermodynamic process, the heat transfer between the solid and the melt must take place in a stable and controlled manner. In the VDS technique pressure and volume of the melt is maintained constant during the process of crystal growth. Thus the enthalpy become heat transfer at a constant pressure. To have stable estimated temperature gradient at the melt-solid interface, the heat ΔH must be conducted away through the growing crystal. But this conduction of heat will depend on thermal conductivity of InSb as well as thermal conductivity of the ampoule wall i.e. the quartz. It is reported that the thermal conductivity of InSb varies with the temperature and at high temperature the thermal conductivity of InSb decreases drastically. At 500 K the thermal conductivity of InSb reduces to approximately < 0.1 W cm^{-1}K^{-1}.

For InSb crystal

$$\frac{\Delta H}{C} = 535 \text{ K} \quad (7)$$

The thermal diffusivity of InSb reported is ≈ 0.16 cm^2/s at 300 K.

$$k_{l,s} = \frac{\lambda}{\rho \cdot C}, \quad (8)$$

where ρ is density and λ is the thermal conductivity.

Thus if the temperature gradient is of the order of 20 Kcm^{-1}, then according to equation (6), the crystallization velocity υ i.e. the growth rate of InSb crystal growth should be:

$$\upsilon < 9 \text{ cm/hr}.$$

But as the crystallization velocity is proportional to the thermal diffusivity, i.e. ability of a material to conduct thermal energy, it is necessary to consider the thermal conductivity (thermal diffusivity) of the am-

poule wall i.e the quartz material. The reason for this is, the solidification is taking place in the ampoule. Therefore the temperature gradient maintained in the furnace is communicated to the crystal material through the ampoule wall.

Thermal diffusivity of quartz ≈ 0.010 cm^2/s, which is approximately $1/10^{th}$ of that of InSb (0.16 cm^2/s at 300 K). Thus the maximum limit on the solidification velocity becomes:

$$\upsilon < 9 \text{ mm/hr.}$$

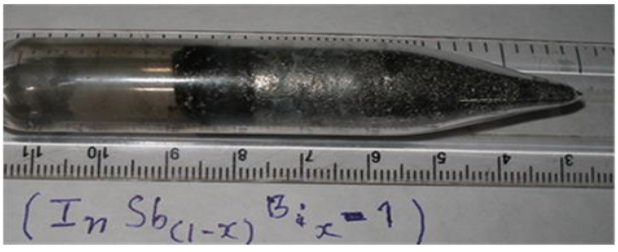
3. EXPERIMENTAL

Crystal growths of InSb based semiconductor crystals from melt were carried out without seed by Vertical Directional Solidification (VDS) technique [10] at the different growth rates < 6 mm/Hr. Since impurity amount of Bi doped is less than 5 % of InSb content in InSbBi composition, the solidification temperature of the material was considered to be 530 °C i.e. melting point of InSb. Hence steady and stable temperature gradient at this temperature in the furnace plays an important role in the crystal growth. Temperature profiles at various set temperatures of the furnace were studied to estimate the temperature gradient at the solid-liquid interface. The growths were carried out at the set temperatures (constant temperature, set at the center of the VDS furnace) 630, 700, 750, 800, 850, 900 and 950 °C for which the temperature gradients were 12, 14, 16, 18, 20, 22 and 24 °C/cm respectively. To obtain cohesive melt in the ampoule, the ampoules were rotated with different rpm. Also during the growth process, in order to intensify stirring effect, the rotation speeds of the ampoules were of the order of 12 rpm. After completion of the growth process and subsequent annealing, the grown ingots were removed from the ampoule. To obtain wafers (substrates) for the characterization, the grown ingots were cut perpendicular to the axis. Further the wafers were cleaned, lapped and polished to mirror finish. The substrates were characterized by microstructures, crystal defects, hardness and electrical mobility.

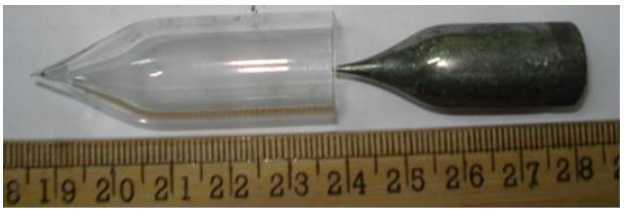
4. RESULTS AND DISCUSSION

4.1 Study of Detachment

Detachment (contactless growth) of the grown ingot from the ampoule wall is one of the parameter to judge quality of the crystal. The detached crystal growths produce good quality crystal with uniform physical parameters such as resistivity, hardness etc. on the polished wafers obtained from these ingots.



a



b

Fig. 2 – As grown crystals grown by VDS mostly attached growth (a) and totally detached growth (b)

Detachment of the grown crystal was observed during the process of removing the ingot from the ampoule. The crystal grown at the temperature gradient 12 °C/cm was mostly attached (Fig. 2a) with the ampoule wall. In this case some gas bubble indentations were present on the surface of the ingots, indicating that the solid grew in contact with the ampoule wall. Total detachment was observed (Fig. 2b) in the growth at the temperature gradient of 22 °C/cm in which, the as grown ingot easily comes out of the ampoule without having stickiness with the ampoule wall. Partial or total detachment of the ingots (growth No 1 to 6) grown at various growth rates and temperature gradients was observed as reported in the Table 1. The detachment was indicated by a clean dull surface. Electrical and optical characterizations of the crystals indicate that the quality of the crystal is better in the detached crystals [11-12].

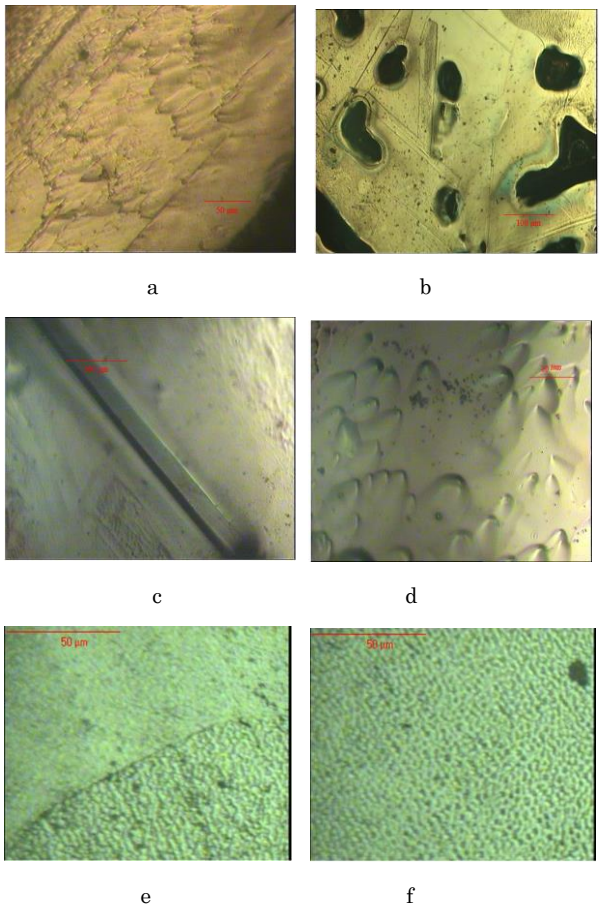
4.2 Microstructures and Defects

The crystal quality was verified by the study of microstructures and defects observed on the etched surface of the wafers by using optical microscope. The ingot of the crystal growth No 1 was grown in contact with the ampoule wall. It consists of cracks due to mechanical stress at the edges of the wafer and propagating from the point where the material is stuck with the ampoule wall as shown in Fig. 3a. Also the etch-pit (Fig. 3d) were observed on the wafer surface with EPD ~ 7×10^6 cm^{-2}. The black spots on the surface shown in Fig. 3b are due to unification the impurity material (bismuth) i.e. inclusions of size 50 ~ 100 μm. A straight, oriented and uniform lamellae growth of width = 18 μm as shown in Fig. 3c is observed in the detached region of growth No 2 indicating uniform growth process [13] and it has reduced defects as compared to the attached growths. Scanning of the surface of the wafers from the detached ingots of the crystal growth No 4 and 6, by optical microscope indicate that, most of the surface is uniform except few impurity clusters Fig. 3f and grain boundaries shown in Fig. 3e. Polished wafers from the detached region of the crystal growth No 2 and 6 shows that, most of the region is free from defects as shown in Fig. 3g and Fig. 3h.

Results of the similar study of wafers obtained from all six growths indicate that, the defects and etch pit density is minimum, and the electrical mobility is maximum (up to 44500 $cm^2/V{\cdot}s$) in the crystals grown at lower growth rate and high temperature gradient. The defects are mostly because of collection of impurity material at that point or voids in the crystal formed by the local heating in the crystal. Such defects are possible

due to excess heat (latent heat of fusion) given out by the solidifying material during solidification at the melt-solid interface and this heat must be transferred to surrounding to avoid the local heating. Effective transfer of the heat between the material in quartz ampoule and surrounding of the ampoule will depend on the conductivity of the material and the quartz, temperature gradient at the solid-melt interface and sufficient time given for the heat conduction by the controlled growth rate. Results of the study of the defect density and the defect size in the six crystals grown at various growth rates and temperature gradients tabulated in Table 1 verify that the crystals grown at low growth rate and high temperature gradient exhibit good crystal quality. Mobility's of the material obtained by measuring resistivity and the Hall coefficient of a wafer from each crystal are also tabulated in the Table 1, which indicate that, the crystal grown at high temperature gradient and slow growth rate have maximum mobility i.e. good crystalline quality.

Surfaces of the polished wafers were scanned by Scanning electron microscope (SEM) to study the texture and microstructures on the wafer surface. Observation of the SEM images in Fig. 4a indicate that, the surface of the growth 1 wafer (attached growth) is a rough surface with large number of surface defects (1.2×10^4 cm^{-2}). There are many lines, curves and dots having compositional defects. Most of the defects are due to gathering of impurity material which is not incorporated in the InSb lattice. Such regions are called domains [14].



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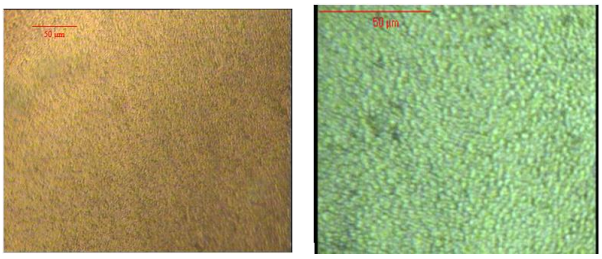
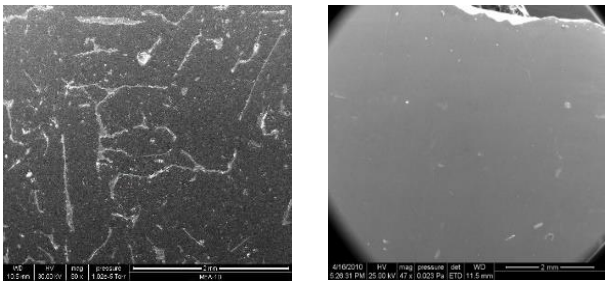


g h

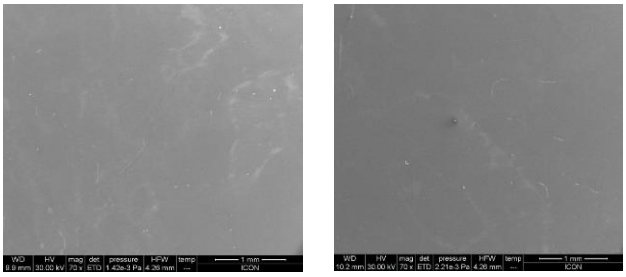
Fig. 3 – SEM of the polished wafers of cracks in crystal growth 1 (a), impurity inclusions in crystal growth 1 (b), lamellae in crystal growth 2 (c), etch pits in crystal growth 3 (d), grain boundary in crystal growth 4 (e), uniform microstructure with one void (black spot) in crystal growth 7 (f), defect free uniform surface in crystal growth 2 (g) and 6 (h)



a b

Fig. 4 – SEM of the polished wafers of crystal growth No 1 (a) and crystal growth No 2 (b)

The Fig. 4b is representing surface of growth 2 wafer from the detached region. Most of the region of the wafer surface is smooth and free from the defects. Since growth 6 and growth 7 crystals were totally detached, the wafer surfaces shown in Fig. 5a, b were expected to have reduction in the defects. Thus surface scanning of the wafers from the six crystal growths show that, there is great reduction in such domains from 1.2×10^4 to 60 (in region of 10 mm × 10 mm) in detached crystal growth carried out at high temperature gradient and low growth rate.



a b

Fig. 5 – SEM of the polished wafers of crystal growth No 6 (a) and crystal growth No 7 (b)

5. CONCLUSION

Growth of InSb based semiconductor crystal from melt is Thermodynamic process which involves large amount of heat transfer between the material and its surrounding during the growth process. Effective removal of unwanted heat is possible by controlling the

Table 1 – Study of microstructures

No	Crystal Growth No	Growth Rate mm/hr	Temperature gradient dT/dz, °C/cm	Detachment	Etch Pit Density cm^{-2}	Mobility μ $cm^2/V{\cdot}s$	Average size of the defects
1	1	6	20	attached	7×10^6	854	≤ 150 μm
2	2	2	24	detached	2.5×10^4	44495	≤ 25 μm
3	3	4	12	partially detached	5×10^4	5919	≤ 75 μm
4	4	3	16	detached	8.3×10^3	4500	≤ 20 μm
5	6	5	14	detached	1.6×10^4	30000	≤ 12 μm
6	7	3	22	detached	8×10^3	21163	≤ 40 μm

temperature gradient at the melt-solid interface and the growth rate well below the estimated rate. Out of six crystals grown at various growth rates and temperature gradients, the crystals grown at higher temperature gradient and slow growth exhibit good crystal quality. Optimized growth rate for the growth of InSb based bulk crystals grown by VDS technique is 2-3 mm/hr when the temperature gradient is of the order of 22 °C/cm.

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