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Growth of uniform $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ bulk crystals by self-solute feeding technique

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Abstract

Compositionally homogeneous, crack-free bulk crystals of $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ with x as high as 0.4 has been grown for the first time using a self-solute feeding method. A balance between the growth rate and the spacing between the solute and the growth interface has been found to be crucial in maintaining uniform alloy composition.

I. Introduction

Substrates of ternary compound semiconductors of GaInSb , GaInAs and InPAs in the band gap range of 0.5 – 0.7 eV are of particular interest for Thermophotovoltaic (TPV) devices [1-4]. The main technical challenge in growing bulk crystals of ternary alloys is mechanical cracking of crystals due to spatial compositional inhomogeneity [5-8]. Cracking can be eliminated by ensuring radial compositional uniformity in the crystals. A planar melt-solid interface shape during growth is necessary in maintaining radial composition uniformity. Due to inherent alloy segregation dictated by the pseudo-binary phase diagrams, the growth interface shifts towards the lower temperatures. Hence if the external temperature gradient imposed by the furnace remains constant, the growth interface shape can change from convex to concave during growth. Temperature gradient and growth rate manipulation and proper melt mixing using forced convection have been found to be effective in maintaining radial homogeneity [9,10]. Furthermore, if the alloy composition in the melt is kept at a constant composition level, the growth interface will automatically remain flat, convex or concave depending on its initial shape. Solute feeding via the double crucible technique has been attempted by previous researchers to grow uniform crystals [7,8]. However, the double crucible method is suitable only for dilute alloy compositions due to technical difficulties. In this paper, we have described a new

method (self-solute feeding) wherein homogeneous ternary crystals of any desired composition could be grown by taking advantage of the fundamental solute diffusion properties in the melt.

II. The Self Solute Feeding Method

The self solute feeding concept is demonstrated schematically in Fig. 1. A molten solvent (melt) is kept in an isothermal furnace. The solute is introduced in the form of a solid piece into the melt. Depending on the temperature (phase diagram), a certain amount of the solute dissolves in the melt. If heat is extracted from the melt in a directional fashion such as in Bridgman growth, solidification occurs. The solid is richer in the higher melting component which happens to be the solute. Hence the melt gets depleted in the higher melting component. However since the melt is kept at the same temperature, the solute dissolution continues to keep the melt at the constant composition. Subsequent cooling of the melt will lead to the same alloy composition in the solid and thus a uniform crystal is obtained.

The process flow for growing homogeneous $\text{Ga}_{0.75}\text{In}_{0.25}\text{Sb}$ is shown in Figure 2. The growth experiment is started with the mole fraction of GaSb and InSb exactly as desired in the final crystal. The temperature of the furnace is heated to the solidus temperature for the desired composition and then the crucible is directionally cooled to grow the crystal. The melt composition is always the liquidus composition and care should be taken to keep the melt isothermal. In this process, the entire charge is not molten to start with. Only a fraction of the charge is in liquid phase depending on the temperature. As growth proceeds, the liquid gets depleted in the one of the binary components which is then replenished from the undissolved solute. In the case of GaInSb growth, the solvent is Ga-In-Sb pseudo-binary liquid and the undissolved solute is GaSb.

Unlike in conventional melt growth, monitoring of the liquid composition is not needed in the self solute feeding technique during growth. The only parameter which needs to be controlled is the growth temperature. The melt should be isothermal since the dissolution rate and hence the solidifying crystal depends strongly on the temperature. The maximum allowable temperature variation to maintain compositional uniformity within 0.5 mol% during the growth of GaInSb can be easily evaluated from the phase diagram. For most of the composition range, the temperature should be controlled within 1 to 2 °C. If the temperature fluctuation exceeds the specified range, the crystal composition will vary. For device application on lattice matched substrates, the composition of the wafer should be controlled within 0.5 mol%. The temperature controllability should be accordingly within 2 °C.

Since the self solute feeding technique requires a near isothermal melt, the driving force for solute transport (and growth) is primarily diffusion controlled. This drastically reduces the growth rate of the alloys. Growth rates in the diffusion controlled regime is typically of the order of 0.1 mm/hr. To enhance the growth rate, the solute was kept within 1 mm of the melt-solid interface. With this arrangement and a thermal gradient ~ 5 °C/cm, the maximum growth rate for inclusion-free single crystals could be increased to 1 mm/hr. Crystals grown with rates above 1 mm/hr had inclusions. As discussed later, any variation in the spacing between the solute and melt-solid interface could lead to significant compositional variations in the axial (and radial) direction. The temperature gradient should be kept in the range of 2 – 5 °C/cm to avoid convection (necessary to maintain constant growth rate), while enabling directional solidification.

The self solute feeding method has significant implications for large area ternary crystals. Due to the intrinsic solute feeding during growth with no external or internal monitoring of the melt composition, the yield of homogeneous alloy composition is 100 %. Moreover, low temperature gradient is needed as opposed to high gradients in the double crucible method, which is beneficial for low defect density crystals. Finally, the process is simple and easily scalable in both open and sealed crucibles.

III. Experimental Results and Discussion

Charge Synthesis and Crystal Growth

Pre-synthesized binary compounds of GaSb and InSb polycrystals (20 mm diameter) were used in all the experiments. Since the aim of these experiments was to test the concept of self solute feeding, no attempts were made to grow single crystals by using seeds. InSb was placed at the bottom of the crucible along with the GaSb feed on the top as shown in Figure 1. The crucible was placed in a uniform temperature zone of a single zone furnace. The hot zone was kept at 5 °C above the solidus temperature. The temperature gradient in the furnace near the bottom of the crucible was approximately 5 °C/cm. Melt was encapsulated by alkali halide salt (LiCl-KCl eutectic mixture). Inert argon gas up to 1.2 atmospheres was used to pressure the melt to avoid volatilization of the group V components during growth.

The experiments were performed in a transparent furnace with gold coated tube around the heaters. Hence the solute dissolution, solidification and the melt-solid interface position could be seen clearly. In the initial stages of heating, the InSb ingot started melting. Dissolution of GaSb was initiated naturally. After the furnace reached the set temperatures (solidus temperature), it took 3-5 hours for

the dissolution of GaSb to stop. A total melt of approximately 1.5-2.0 cm was synthesized in each experiment. At the end of the initial dissolution, there was enough length of GaSb feed left to enable further dissolution. No melt stirring was performed during the entire experiment. The melt was equilibrated for 2 hours and then the crucible was lowered at a rate between 0.5 mm/hr to 3 mm/hr in different experiments. During various experiments, the spacing between the solute feed and the melt-solid interface was varied by pulling out the feed from the melt. Figure 3 shows the crystalline structure of homogeneous $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ grown in a flat bottom crucible without seed. The polycrystalline boule was grown at 600 °C. No cracks were observed in the grown crystals.

Compositional Analysis

Electron microprobe X-ray analysis (EPMA) was performed to determine the axial composition in the crystal. Thin slices of the crystals were used for the EPMA measurements. The maximum sample size that could be inserted in the EPMA set-up was 1.5 cm. The samples were mirror polished on both sides for the EPMA measurements.

The effects of growth temperature, growth rate and solid-liquid interface shapes on the alloy composition and its radial variation are shown in Figures 4, 5 and 6, respectively. The GaInSb alloy compositions grown at 610 and 630 °C (shown in Fig. 4) are consistent with the solidus temperature in the GaSb-InSb pseudo-binary phase diagram. The growth rate influences the microstructure of the grown crystals. Higher growth rates lead to larger compositional variations as depicted in Figure 5 and inclusions in the crystals as shown in Figure 7. The inclusions are introduced by interface breakdown due to super-cooling near the solid-liquid interface (the boundary layer). This implies the growth rates for mixed alloys has to be close to 1 mm/hr or lower.

As mentioned earlier, the solid-liquid interface shapes are very critical for uniform radial compositional homogeneity. The isothermal melt-solid interface concave towards the solid means the radial compositional profile in the crystal to be convex with respect to the solid. Thus, the center of the wafer has higher solute content compared to the edges. For single crystal growth, concave melt-solid isotherms are highly undesirable as they lead to spurious nucleation on the walls of the crucible and lead to multiple grain or polycrystal structure. Moreover, extended defects such as dislocations move normal to the melt-solid interface and grow into the crystal thus increasing the defect density in the wafers. A planar solid-melt interface is the most ideal one and leads to uniform alloy composition. Figure 6 shows the radial alloy composition for three wafers taken along the boule. The radial profile varies along the length of the crystal indicating change in interface shape during the growth. The interface shape depends on its location in the furnace. Convex isotherms are located in the hot zone of

the furnace and concave in the cold zone, as determined by the heat flow profiles from the crucible-melt-solid system to the furnace system. A planar interface is located between the hot and cold zones. In experiments presented below, we varied the hot zone temperature to obtain a planar interface during growth of graded composition regions in the crystal. The radial composition profiles in these crystals were flat within the limit of experimental error (Figure 8). Hence we plotted the axial profiles to demonstrate the effect of spacing between the solute and melt-solid interface.

Figures 9 to 12 show the axial profiles of GaInSb grown from different initial melt compositions. The graded regions in the crystals were obtained by removing the GaSb solute from the melt after the initial dissolution. Constant regions were obtained by placing the GaSb feed within 1 mm from the growth interface. The importance of spacing between the growth interface and the solute in achieving axial compositional homogeneity is shown in Figures 11 and 12. In the crystal shown in Fig. 11, when the solute distance was decreased to 0.5 mm keeping the growth rate constant at 1 mm/hr, the indium composition is found to be lower. When the spacing was set back to 1mm, the indium concentration increased to its original level. Similarly in Fig. 12, fluctuations in the indium concentration around 12 mol% is due to repeated and intentional variations in the spacing between the solute and growth interface. During the graded growth between 12 and 15 mol%, the solute was removed from the melt. When the solute was inserted back (at 15 mol%), the composition was found to be constant as expected.

IV. Conclusion

Diffusion of solute in the melt has been advantageously used for growing uniform crystals of GaInSb by a self-solute feeding method. Crack-free crystals of concentrated GaInSb alloys with indium content as high as 40 mol% has been grown for the first time using this method.

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Figure 1. Self Solute feeding technique for growing homogeneous mixed crystals. The solute feeding set-up is shown separately on the right.

Figure 2. Process flow for growing homogeneous $\text{Ga}_{0.75}\text{In}_{0.25}\text{Sb}$ using the self solute feeding technique

Figure 3. Grain Structure in homogeneous $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ grown in a flat bottom crucible without seed

Nucleation Temperature: 610 °C

Nucleation Temperature: 630 °C

Figure 4. Effect of nucleation temperature on the first to freeze GaInSb alloy composition

Growth Rate: 3 mm/hr

Growth Rate: 1 mm/hr

Figure 5. Effect of growth rate on the radial variation in alloy composition

Figure 6. Effect of solid-liquid interface shape on the radial composition profile of GaInSb

Figure 7. Effect of growth rate on the microstructure of GaInSb (growth rate: 3 mm/hr)

Figure 8. Radial indium profile in the crystal confirming flat solid-melt interface shape

Figure 9. Effect of solute feeding on the axial indium profile in GaInSb

Figure 10. Effect of solute feeding on the axial indium profile in GaInSb

Figure 11. Effect of spacing between solute and growth interface on the axial indium profile in GaInSb

← Growth Direction

Figure 12. Effect of spacing between solute and growth interface on the axial indium profile in GaInSb