Growth of gallium antimonide by vertical Bridgman technique with planar crystal–melt interface

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Abstract

High quality single crystals of GaSb were grown using vertical Bridgman technique with a planar melt–solid interface. Various factors affecting the interface shape during growth were investigated. In general, the shape of the freezing isotherm was found to depend on the furnace temperature profile near the melt–solid interface, the ampoule lowering rate, the ampoule geometry, the mode of heat extraction from the tip of the ampoule and the extent of lateral heat loss from the side walls of the ampoule. A critical ratio of temperature gradient of the furnace at the melting point to ampoule lowering rate was found to be necessary for planar interface shape during the growth. The sensitivity of the interface shape was found to decrease with increasing temperature gradient of the furnace and ampoule diameter. Crystals grown by employing the flat melt–solid interface exhibited superior quality than those with non-planar interfaces.

1. Introduction

GaSb is an important III-V compound semiconductor material for optoelectronic applications in the range of 0.3 to 1.58 eV [1]. The quality of an epitaxial layer and the yield of devices made from it mainly depend on the structural perfection of the substrate. The Bridgman growth of high-quality crystal requires careful control of the thermal conditions. The solid–liquid interface shape is an important factor in this technique. A convex freezing isotherm (relative to the solid) will often produce a high percentage of single crystal material [2], but where segregation is important, a flat freezing isotherm will give the best radial uniformity. Although grain selection is favored by a convex shape, such an interface enhances twin generation during growth [3]. Thermal stresses, which can generate dislocations, are minimal for a planar interface. Theoretical modelling of crystal growth by the vertical Bridgman–Stockbarger technique with a two-zone furnace has been carried out by a large number of workers, both analytically (refs. [4–9] and references therein) and numerically (refs. [10–16] and references therein). Relatively few experimental efforts have been made [17–21] to check the consistency of these theoretical predictions. In this paper, we present the results of extensive growth experiments carried out in our laboratory with the aim of obtaining high-quality...
single crystals of GaSb by vertical Bridgman technique with the planar melt–solid interface. A single-zone vertical Bridgman furnace was used for our studies. A more general analysis of the heat flow problem based on accepted theoretical principles is presented, which permits quantitative conclusions to be drawn regarding the solid–liquid interface shape, its dependence on various system parameters and its sensitivity to perturbations.

2. Experimental procedure

A “Metal Research” BCG 365 crystal growth system with a single zone resistively wound tubular furnace, of 21 cm length and 2.5 cm diameter, was used for our growth experiments. A schematic diagram of the furnace and the crucible system used in the present study is shown in Fig. 1a. The furnace was controlled by a Eurotherm PID temperature controller with an accuracy of ±1°C. The heater and the crucible assembly were enclosed in a double-walled cylindrical chamber which was evacuated to 10⁻³ Torr throughout the growth experiments to minimize convective heat losses. The double-walled jacket was cooled by continuous circulation of water (flow rate: 4 litres/min). The procedure for synthesis of GaSb and subsequent growth of single crystals were earlier reported by us [22].

Initial experiments were aimed essentially at obtaining single crystals, for which purpose various shapes of tip of the ampoules (Figs. 1b, 1c and 1d) were used. The tip shape shown in Fig. 1d was found to be better as single crystals were always obtained by employing this shape. The cone angle (Fig. 1) was changed in the range of 20°–45° to check whether the angle had any influence on crystallinity. However, no influence was noticed and the grown crystals were always single crystals. To check whether diameter variation leads to polycrystallinity (as reported by Roy and Basu [23] and Hársy et al. [24]), crystals were grown with diameters ranging from 0.8 to 1.2 cm. We did not find any deviation from single crystallinity. In order to avoid Sb volatilization from the upper end of the crystal during growth, the

ampoule was placed in such a way that its top was always at a higher temperature than any other parts. With the motivation of growing high quality crystals employing the flat melt–solid interface, we evaluated various growth conditions which could lead to the desired interface shape. The results of these studies will be discussed in detail in the next section.

3. Results

Although interface shapes in Bridgman growth may be complex, the most common shapes are parabolic. The interface shape is described by the terms convex, concave or planar with respect to either melt or crystal. In this paper, the term convexity will be used to describe quantitatively...
the interface shape. If the radius of the ampoule is \( r \) and the height of the arc is \( h \), then we define the convexity \( h_c \) (see Fig. 1b) as

\[
h_c = h/r.
\]

If the interface shape is convex (seen from the solid), \( h_c \) is positive. If it is concave, \( h_c \) is negative; zero convexity represents a planar interface shape. In our experiments, the melt–solid interface shapes were determined by observation of the shape at the top of the grown crystal (Fig. 2). Interface demarcation experiments were separately done to reveal the interface shape by rapidly quenching and subsequently etching the grown crystals cut along the growth axis. The interface shape was found to replicate the shape of the crystal at the top end and was found to be almost identical throughout the length of the crystal.

3.1. Effect of furnace temperature gradient and ampoule lowering rate

A large number of growth experiments were carried out using different furnace temperature gradients \( (G) \) and varying ampoule lowering rates \( (V) \). Fig. 3 shows the various temperature profiles obtained by changing the input power to the furnace. The profiles are characterized by their slopes at the melting point of GaSb \( (712^\circ \text{C}) \). The temperature gradients \( (G) \) used in our studies varied from 20 to \( 80^\circ \text{C/cm} \) at \( 712^\circ \text{C} \). The need to limit maximum furnace temperature to \( T < 1000^\circ \text{C} \) prevented us from operating on the steeper temperature profiles. The ampoule lowering rates employed ranged from 1 to 5 mm/h. Lowering rates exceeding 4 mm/h lead to void formation on the crystal surface in contact with the ampoule and produce strain in the grown crystals. Hence, lowering rates in excess of 4 mm/h were not pursued further. The convexity observed for various temperature gradients and ampoule lowering rates are shown in Fig. 4. For very low translational rates, the interface shape was found to be planar for crystals grown using shallow temperature gradients, whereas it was convex when high temperature gradients were employed. For the shallow profiles 1, 2 and 3 with temperature gradients 21, 37 and \( 44^\circ \text{C/cm} \), respectively, the interface shape remains virtually flat until a “critical lowering rate” is reached above which the interface starts becoming increasingly convex with increasing velocity. It should be noted that this critical lowering rate occurs at a higher value and the rate of increase of convexity with increasing velocity becomes less as the temperature gradient of the furnace is increased (see Fig. 4). However, for the steeper profiles 4 and 5, an opposite trend was observed, i.e., the interface convexity was found to decrease as \( V \) was increased. At higher translational rates, the interface shape was planar for the steeper profiles and convex for the shallower ones. These

![Temperature profile graph](image-url)
results indicate that a flat isotherm should be obtainable by a suitable choice of furnace temperature profile and ampoule lowering rate.

3.2. Effect of ampoule stem conductivity, melt thermal conductivity and ampoule geometry

Apart from the temperature gradient of the furnace and the ampoule translational rate, we also evaluated the effect of various other parameters such as the ampoule geometry, melt composition, ampoule stem conductivity, etc. on the interface shape. It was found that the contributions due to these factors were much less. Below, we briefly discuss the effects of these factors.

Quartz wool, syndanite, stainless steel, brass and copper having increasing order of thermal conductivity were separately used to vary the heat extraction from the tip of the ampoule. Special care was taken to avoid any change in furnace temperature profile due to the thermal conducting stem. This was done by covering the sides of the stem material with a thick layer of high insulating material like quartz wool. Increasing the thermal conductivity of the stem increases the convexity, as shown in Fig. 5.

To evaluate the dependence of thermal conductivity of the melt on interface shape, growth from gallium-rich and antimony-rich melts were carried out. Growth from Ga-rich melts leads to more convexity than that from Sb-rich melts. The magnitude of the variation was of the same order as in the above case.

The effect of ampoule geometry (diameter and cone angle) on the interface convexity was investigated. For similar growth conditions, the convexity was found to increase with the increase in the cone angle of the ampoule. The effect of heat transfer from the side walls of the ampoule on interface shape was studied by either varying the ampoule wall thickness or covering the sides with quartz wool or kwoool blanket. Slight decrease in convexity was observed in both the cases. Under all growth conditions, the convexity observed was always more for a smaller diameter ampoule.

3.3. Critical value of $G/V$ for planar interface

It is apparent from the above experimental results that the dominant factors which vary the interface convexity are $G$ and $V$. All other factors have secondary contributions. Keeping this in view, several experiments were performed to obtain a planar interface by varying either $G$ or $V$.

![Image](image_url)

*Fig. 4. Effect of furnace temperature gradient ($G$) and ampoule lowering rates ($V$) on interface shape (ampoule diameter, 1 cm; cone angle, 30°; stem, syndanite; melt composition, Ga/Sb = 1; crystal length, 5 cm).*

![Image](image_url)

*Fig. 5. Effect of thermal conductivity of ampoule stem on interface shape ($G = 44^\circ$C/cm, $V = 2.5$ mm/hr). Values of stem thermal conductivity in W/cm°C are: quartz wool, 0.00366; syndanite, 0.002076; stainless steel, 0.242; brass, 1.384; copper, 3.547.*
It was found that a critical value of $G/V$ was necessary for obtaining the planar interface. This value in our case was evaluated to be 230°C h/cm² (Fig. 6). However, only a slight variation of the critical value of $G/V$ was observed due to the variation of above-mentioned secondary factors. Moreover, any deviation from the critical $G/V$ always resulted in a convex interface, the convexity being more in case of smaller ampoule diameters and shallow temperature gradients, indicating the sensitivity of the interface shape on these factors.

3.4. Characterization of the grown crystals

Crystals grown by flat interface exhibited extremely low dislocation densities due to reduction in thermal stress at the interface. An overall reduction of dislocation densities by an order of magnitude was observed. The average dislocation density for crystals grown with flat melt–solid interface was approximately 50 cm$^{-2}$ as compared to $10^3$ cm$^{-2}$ for the crystals grown with convex interfaces. Electrical characteristics of Schottky diodes fabricated on crystals grown by flat interface were much superior to those fabricated on crystals grown by convex interface. Capacitance–voltage and Hall measurements revealed relatively homogeneous impurity distribution for the crystals grown by planar interface. Current–voltage measurements exhibited sharper reverse breakdown for diodes fabricated on crystals grown with flat isotherm. Details of these characterization studies will be published elsewhere.

4. Discussion

The present work on GaSb had its primary objective as the growth of single crystals with planar melt–solid interface. Initially the efforts were to obtain single crystals. This was achieved by the proper modification of the ampoule tip. However, attainment of planar melt–solid interface required a detailed investigation of various factors influencing the interface shape. Below we discuss the probable reasons that led to various melt–solid interface shapes during our growth experiments.

For a vertical Bridgman system, one can draw the following inferences regarding the melt–solid interface shape from the heat balance analysis for a steady-state condition [21]. For a uniform temperature gradient with melt and solid thermal conductivities $K_m$ and $K_s$, respectively, one expects a convex, concave or flat melt–solid interface depending on whether $K_f < K_s$, $K_f > K_s$ or $K_f = K_s$. However, for non-uniform temperature gradients, reducing the temperature gradient above the interface and/or increasing the temperature gradient below the interface could make the interface shape convex even if $K_f > K_s$. Similarly, for $K_s > K_f$, a concave interface can be obtained by reducing the temperature gradient below the interface and/or increasing the temperature gradient above the interface. For a flat interface, the radial heat flux near the interface must be zero. This requires the temperature profile of the furnace to be such that the axial heat flow above the interface is equal to that below the interface. Hence, by proper modification of the furnace temperature gradient, it is possible to alter the melt–solid interface shape to our advantage.
In addition to the temperature gradient, the motion of the ampoule through the furnace shifts the position of the isotherms, thereby affecting the shape of the interface [4,12]. With increase in velocity, the convex isotherms tend to become less convex, the concave isotherms more concave and the planar isotherm shifts upwards and occurs at higher temperatures. Sukannek [5] performed an analytical calculation to determine the deviation of freezing rate from translation rate in case of very low ampoule velocities in a two-zone furnace separated by an insulation layer. It was found that the interface velocity approaches the ampoule velocity as the width of the insulation layer is decreased. Fu and Wilcox [12] demonstrated that by increasing the width of the insulation layer, the radial temperature gradient and the sensitivity of the interface shape to parameter changes in the system reduces, thereby producing a planar interface easily. However, in the case of shallow gradients, the interface velocity is more difficult to control and a higher ratio of interface to velocity results as depicted by Sukannek. The increasing width of the insulation layer in the above cases is equivalent to reducing the temperature gradient of the furnace near the melt–solid interface and vice versa for our experimental situation.

Using the above concepts, our experimental results can be explained as follows. The case of shallow and steep temperature profiles will be considered separately. As mentioned above, the interface shape mainly depends on the temperature gradient below and above the interface. The condition \( K_f G_f \sim K_s G_s \) is satisfied for the shallow profiles 1, 2 and 3. Here \( G_f \) and \( G_s \) are the temperature gradients in the melt and solid, respectively, near the interface. Hence a planar interface is observed (Fig. 4). With increase in velocity, the growth rate exceeds the translational rate, thereby raising the interface position towards the high-temperature zone of the furnace. This results in a convex interface. In case of the steeper profiles 4 and 5, the condition \( K_f G_f < K_s G_s \) is satisfied and hence a convex interface is expected. As the interface velocity and the translational rate are the same in case of steeper profiles, there is relatively no shift in interface position. Increasing velocity leads to decreasing convexity, as depicted by Fu and Wilcox. The observation of a critical \( G/V \) (Fig. 6) for obtaining planar interface shape can be well understood by the above argument.

Let us now briefly discuss the influence of secondary factors on the melt–solid interface shape. Varying the ampoule geometry and surroundings alters the radial heat flux and the end losses as a result of which the interface shape changes. Increasing the diameter leads to (i) increase in the amount of radiative heat loss through the surface compared to heat conduction through the charge and (ii) decrease in radiative heat losses from the ampoule surface to the ambient lying below the furnace edges (which is equivalent to decreasing the furnace tube diameter). Both these result in decreased convexity, as observed in our experiments. Increasing the cone angle increases the heat loss by radiation from the lower end of the ampoule to the cooler regions of the furnace during the initial stage of growth. Similarly, increasing the conduction of heat from the tip of the ampoule by using higher thermal conductivity stem results in greater heat losses from the lower end of the ampoule. Both these result in an increase in convexity. Increasing the effective thickness of ampoule by covering the sides with high-insulating material like quartz wool flattens the temperature profile in the material specially near the interface, which tends to make the interface less convex.

The effect of changing thermal conductivity of the melt–solid interface is to alter the overall axial heat conduction through the material. Gallium-rich melts, being more metallic in nature than antimony-rich melts, possess higher thermal conductivity. This leads to a more convex interface in the case of the Ga-rich crystals than the Sb-rich ones.

Until now, we have discussed those factors which can affect the melt–solid interface shape. It is also important to know the sensitivity of the interface shape and position to the thermal conditions prevailing inside the furnace. Analytical calculations of Chang and Wilcox [4] and Sen and
Wilcox [7] showed that the sensitivity of interface shape and position to thermal conditions decreases as:

(i) the maximum operating temperature of the furnace increases;
(ii) the diameter of the ampoule increases;
(iii) the width of the insulation zone decreases (larger furnace temperature gradient near the interface in our case);
(iv) the thermal conductivity of the material decreases.

Our experimental observations are in good agreement with their theoretical predictions. Planar interface with low sensitivity was obtained by imposing the above-mentioned criteria.

5. Conclusions

In summary, we have evaluated various factors affecting the melt–solid interface shape during growth. The planar interface shape was effectively used to grow high-quality single crystals. Our experimental findings are more general and can be applied for the vertical Bridgman growth of other materials as well. Recent heat transfer calculations performed by us agree well with the experimentally observed values and will be published elsewhere.

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References