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Stability of planar crystal–melt interface during vertical Bridgman growth of gallium antimonide

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Abstract

The stability of planar crystal–melt interface shape during the growth of gallium antimonide (GaSb) by vertical Bridgman technique under different experimental conditions has been evaluated. To achieve planar melt–solid interface, a critical ratio of temperature gradient of the furnace at the melting point (G) to ampoule lowering rate (V) was found necessary. The value of G/V was found to deviate as a result of perturbation in various experimental parameters such as the melt thermal conductivity, 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. Nevertheless, the G/V values were found to lie in a narrow range in our experiments. Expectedly, crystals grown by employing the flat melt–solid interface exhibited superior quality than those with nonplanar ones.

Keywords: Gallium antimonide (GaSb), melt–solid interface, vertical Bridgman technique, crystal growth.

1. Introduction

GaSb is an important III–V compound semiconductor material for optoelectronic applications. It has been increasingly used recently, as a substrate material for the fabrication of Sb-based lattice-matched epitaxial layers in the band gap range of 0.3 eV (InGaAsSb) to 1.58 eV (AlGaSb)[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 compositional homogeneity, generation and propagation of defects during growth, defect structure and stress distribution in the grown crystal from which the substrates are made are dictated by the melt–solid interface shape during growth. A planar interface is highly desirable to grow defect-free crystals. In a previous paper[2], we had discussed various factors which affect the crystal–melt interface shape during growth of GaSb by vertical Bridgman technique. It was found that the dominant factors which vary the interface shape are the furnace temperature gradient (G) and the ampoule lowering rate (V). Based on these results, crystals with planar melt–solid interface were grown employing a critical G/V value. It was also mentioned that there is slight variation in the critical value of G/V due to the variation of various other experimental factors like ampoule diameter and cone angle, thermal conductivity of the melt and ampoule stem and the extent of heat transfer from the ampoule walls. In this communication, we elaborate and quantify the influence of these parameters on the interface planarity.

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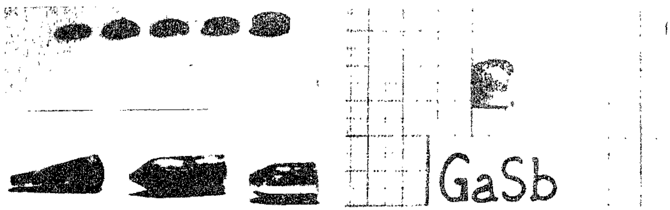


a. b.

FIG. 1.a. Typical crystals grown with convex and planar interface along with the top portion of the crystals with various degrees of convexities. b. a crystal with demarked interface,

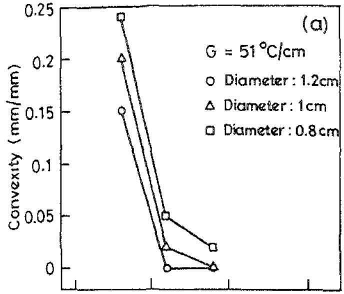
2. Experimental

A Metal Research BCG 365 crystal growth system with a single zone resistively wound tubular furnace was used for our growth experiments. The furnace was controlled by a Eurotherm PID temperature controller with an accuracy of $\pm 0.1°$ C. The procedure for the synthesis of GaSb and subsequent growth of single crystals was earlier reported by us[3]. Further, to improve the quality of the crystals, we investigated various growth conditions which could lead to planar melt–solid interface. The experimental procedure for the determination of interface shape was reported earlier[4]. The interface was found to be either convex (towards the melt) or planar in our experiments. The term convexity (defined as the ratio of height of interface curvature to the ampoule radius) has been used to quantify the interface shape[2]. Figure 1 shows the crystals grown with various interface shapes and a crystal with demarked interface. The deviation in the critical G/V value due to various experimental factors has been evaluated and is discussed below.

3. Results and discussion

The effect of ampoule diameter on the interface convexity is shown in Fig. 2 for two furnace temperature gradients. As can be seen from the figure, larger diameter leads to less convexity. The reduced convexity is due to increase in radiative heat transfer from the surface compared to heat conduction through the charge[5]. Furthermore, the difference in convexity observed for the same variation in diameter is larger in case of low-temperature gradient. This shows that the sensitivity of the interface shape increases with decrease in G as predicted[6]. Increasing the cone angle of the ampoule tip leads to increase in convexity as shown in Fig. 3. The effect of ampoule diameter is also evident from this figure. The enhanced convexity due to increasing cone angle is a result of higher radiation loss from the lower end of the ampoule to the cooler regions of the furnace[7].

The influence of heat transfer from the side walls of the ampoule on the interface shape was evaluated by increasing the ampoule wall thickness or by covering the sides



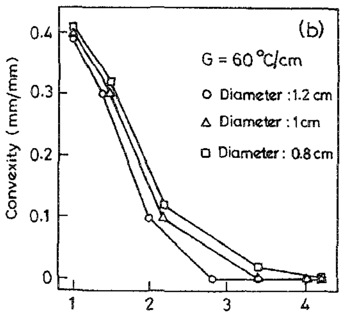


FIG. 2. Convexity *vs* ampoule translational rate. Note the sensitivity of the interface shape on ampoule diameter and temperature gradient.

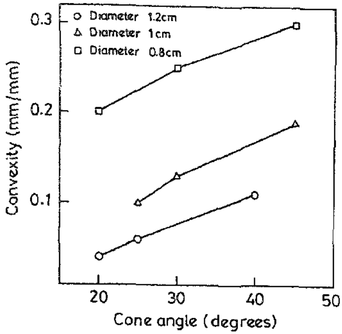


FIG. 3. Effect of ampoule cone angle on interface shape (G: 37°C/ cm, V: 3 mm/h).

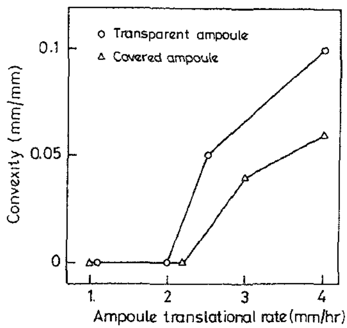


FIG. 4. Influence of effective ampoule thickness on interface shape (G: 44° C/ cm).

with quartz wool or Kawool blanket. Slight decrease in convexity was observed as a result of this (Fig. 4). This is expected because by increasing the effective thickness of the ampoule, the heat conduction in the ampoule increases due to which the temperature profile in the material specially near the interface tends to flatten. It is known that the interface shape is decided by the condition $K_l\ G_l \geq K_s G_s$ where K_l and K_s are, respectively, the thermal conductivity of melt and solid, and G_l and G_s are the temperature gradient in the melt and solid near the interface. Since $K_l > K_s$ for GaSb, decrease in temperature gradient near the interface will tend to make the interface less convex.

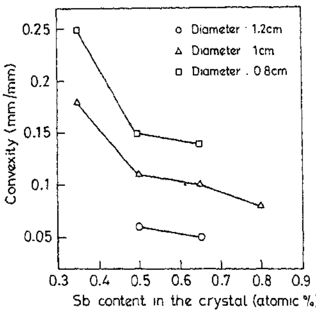


FIG. 5. Effect of melt composition on interface shape (G: 37° C/cm, V: 3 mm/h).

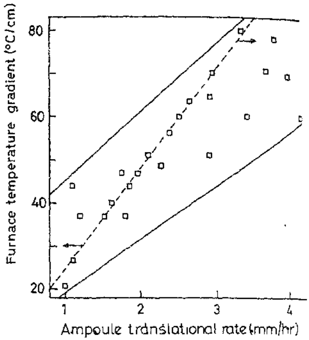
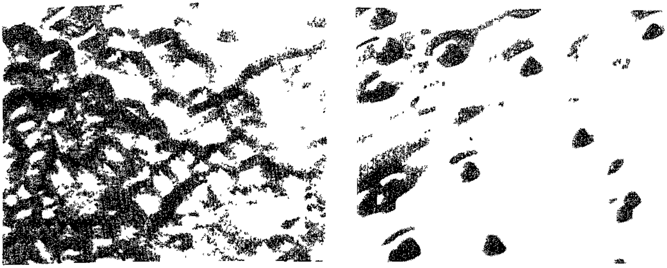


FIG. 6 Furnace temperature gradients *vs* ampoule lowering rates for planar interface. The experimental values of G and V are shown by open squares.

To evaluate the effect of thermal conductivity of the melt on interface shape, growth from gallium- and antimony-rich melts was carried out. Increase in Sb content in the melt resulted in decrease in convexity (Fig. 5). By changing the melt stoichiometry, the thermal conductivity of the melt/solid gets altered. As a result, the overall axial heat conduction through the material varies. Ga-rich melts possess higher thermal conductivity by virtue of it being more metallic than Sb-rich melts. High thermal conductivity leads to enhanced heat conduction. Hence more heat has to be supplied from the radial direction to compensate for the axial heat loss. This leads to increase in convexity. Once again, this figure also shows the effect of ampoule diameter on interface convexity.

To obtain planar interface, a critical value of G/V was found necessary[2]. This value was evaluated to be 230°C h/cm^2 from the slope of the dashed line in Fig. 6 for a stoichiometric composition with a specific ampoule geometry (diameter: 1 cm, cone angle: 30°) and syndanio as the ampoule stem. Any variation in the above-mentioned parameters can lead to departure from planarity. In such cases, the planarity of the interface can be restored by deviating from the dashed line. To explain this let us consider an example. We have seen from Figs 2–5 that decreasing the ampoule diameter leads to increase in convexity. Hence, if the diameter is decreased from 1 to 0.8 cm, any value of G and V on the dashed line will result in a convex interface. To obtain a planar interface, we have to choose values of G and V lying on either the left or right side of the critical line. As discussed in our previous paper[2], for shallow temperature gradients, with increase in ampoule velocity, convexity increases, whereas in the case of steep temperature profiles, increase in ampoule velocity leads to decrease in convexity. Hence, for low values of G and V, a convex interface can be transformed into a planar one by choosing values of G and V which lie on the left side of the dashed line as shown by an arrow in Fig. 6. For higher G and V values, this can be done by shifting towards the right side of the line.



a b

FIG. 7. Dislocation etch pits in crystals grown by (a) convex interface, and (b) flat interface (magnification: 300×).

The same argument can be extended to other cases like increase in thermal conductivity of the ampoule stem and melt and ampoule cone angle which lead to departure from planarity. The trend observed here is quite general and can even be applied to situations where concave interfaces are observed. However, for this case the direction of the arrows will be opposite to that shown for convex interface. It should be noted that the deviations in G/V values caused by the above-mentioned experimental parameters still lie within a narrow range as indicated in Fig. 6 by two solid lines.

4. Characterization of the grown crystals

Crystals grown with flat interface exhibited dislocation densities lower than those grown by convex interface (Fig. 7). This is due to reduction in thermal stress at the interface. An overall reduction of dislocation density by an order of magnitude was observed. It should be emphasized that the high quality of crystals grown by flat interface proved

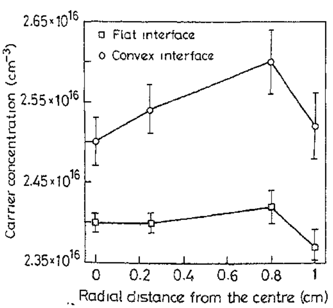


FIG 8. Average carrier concentration profile along the radial direction measured by capacitance–voltage and Hall technique for Te-doped crystals. Variation in carrier concentration along the length of the crystal lie within the error bars.

to be extremely advantageous for device fabrication. 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 (Fig. 8). The sharp fall in carrier concentration at the periphery of the crystal (as shown in Fig. 8) is attributed to the gettering effect by dislocations which are in higher concentration at the periphery of the crystal due to thermal stresses.

5. Conclusion

In conclusion, 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. In particular, we have quantified the effects of ampoule geometry, melt thermal conductivity and the extent of heat transfer from the ampoule walls on the stability of planar interface shape. It is noted that the values of G/V required for obtaining planar interface lie in a narrow range.

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