Suppression of cracks in In$_x$Ga$_{1-x}$Sb crystals through forced convection in the melt

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Abstract

It was demonstrated that forced convection or mixing in the melt during directional solidification of bulk In$_x$Ga$_{1-x}$Sb (0 < x < 0.1) ternary alloys significantly reduces cracks in the crystals. In this study, the enhanced mixing in the melt was generated by a rotating submerged baffle. The resultant improvement in spatial compositional homogeneity lowers the strain gradient or chemical stresses; thus eliminating cracks. The results presented are generally beneficial and should also improve the crystalline quality of other mixed alloys.

Keywords: Suppression of cracks; Forced convection; In$_x$Ga$_{1-x}$Sb crystals

1. Introduction

The III—V ternary alloy system GaSb—InSb covers an interesting band-gap range from ~0.73—0.17 eV [1]. This particular regime is promising for several future devices; in particular, lasers and photodetectors for optical communication beyond 2 µm with nonsilica fibers [2], and high-efficiency thermophotovoltaic (TPV) cells operating in conjunction with low-temperature black body sources [3]. At present, the device structures are fabricated on thin epitaxial layers of ternary alloys grown on binary substrates with suitable buffers to circumvent the lattice mismatch related problems [4]. Availability of ternary substrates would significantly simplify the fabrication cycle, as the devices will be made either on diffused junctions or lattice-matched epilayers. Hence, the overall cost of the final device will be reduced. However, growing bulk crystals of ternary alloys remains an experimentally difficult task [5]. The most common problem encountered is the formation of cracks in the crystals due to spatial compositional inhomogeneity induced by alloy segregation [5]. The present work aimed to (1) grow compositionally homogeneous crystals, and (2) to suppress cracks; even though the problems are interrelated and coupled to some extent.

The binary compounds GaSb and InSb are completely miscible, both in liquid and solid phases.
throughout the composition range; thereby alloying the physical properties of the ternary alloy In$_x$Ga$_{1-x}$Sb to vary with composition [6]. However, the tetrahedral radii of the two substituting atoms Ga and In differ by approximately 12.5% [7]; hence, it is extremely difficult to prepare a homogeneous material [8]. The main difficulty during large crystal growth of mixed alloys from melt arises from the large solidus–liquidus separation [9] and the related segregation and interface breakdown phenomena. During growth, the rejected solute molecules (InSb in this case) accumulate in front of the interface and spread into the liquid phase by diffusion and mixing induced by convection. As a result, spatial compositional inhomogeneity exists in the grown crystals. This, along with the wide difference in the lattice constants and the thermal expansion coefficients of the two binary compounds [5] introduces considerable strain, and invariably leads to cracking of the crystals. Cracking is generally inevitable when the misfit strain gradient exceeds 1% [5]. However, cracking may occur for less than 1% misfit strain gradients with large thermal gradients [5].

The macroscopic cracks can be somewhat eliminated by zone leveling [5], slow cooling [10] or prolonged annealing of the solidified ingot [8]. However, the concentration gradient does not smoothen by thermal treatment [5] as in II–VI compounds, where the diffusion coefficients are 1000 times higher than in III–V compounds. Hence, microscopic cracks still remain. Extreme care in cutting and polishing these alloys is required to avoid fractures. In essence, by improving spatial compositional homogeneity during growth, macro- and micro-crack formation can be avoided.

The most rigorous work on single crystalline growth of ternary alloys has been carried out by Bonner and co-workers [11–13], on the In$_x$Ga$_{1-x}$As system. By employing the “Bootstrapping” technique in the Czochralski (CZ) method they grew crack-free, uniform single crystals of In$_x$Ga$_{1-x}$As up to $x = 0.12$; from large melts with strong mixing induced by counter rotating melt and seed. They emphasized using near-lattice-matched seeds of ternaries (obtained from successive growth runs) for growing crystals beyond $x = 0.05$. The same approach has been used for the growth of In$_x$Ga$_{1-x}$Sb up to $x = 0.05$ with the solute feeding CZ technique [14]. Reasonably good-quality crystals of 10 mm in diameter up to $x = 0.05$ with uniform radial composition have been grown by Garandet et al. [15] by the vertical gradient freeze (VGF) technique. Beyond $x = 0.05$, a large number of cracks, sub-grains, and a high dislocation density were observed.

In this work, the submerged heater method (SHM) was used, a technique developed by Ostrogorsky [16] and successfully demonstrated to grow uniformly doped crystals of Ge, InSb, Sn–Bi dilute alloys, and GaSb [17–19]. In this study, the submerged baffle was used to promote melt stirring by forced convection. As a result of enhanced mixing, the compositional gradient was smoothened and cracks are avoided during growth. It has also been demonstrated that relatively high growth rates can be employed without causing interface breakdown, and a larger fraction of the melt can be solidified before breakdown. In general, controlled stirring has been found to be beneficial in many crystal growth processes [20–29]. In particular, enhanced melt mixing by coupled vibrational stirring improved the chemical homogeneity in Bridgman grown crystals [29].

2. Experimental details

Synthesis of In$_x$Ga$_{1-x}$Sb has been carried out in a multi-zone Mellen furnace (Fig. 1) in 32 mm diameter silica crucibles from pre-synthesized GaSb and InSb freshly etched with CP4 etchant (CH$_3$COOH : HF : HNO$_3$ in 3 : 3 : 5 by volume). For the synthesis of GaSb and InSb, 6N pure In, Ga, and Sb were used without any chemical treatment. The unseeded directional solidification was done in flat bottom or conical tipped silica crucibles of 20 and 32 mm in diameter. Liquid encapsulation of the melt was provided by LiCl : KCl eutectic (58 mol% : 42 mol%) alkali halide salt to avoid volatilization and to reduce the probability of multiple nucleation from the crucible wall [19]. A pre-growth baking of the charge and the salt (to remove moisture) was carried out at approximately 300°C for a period of 10–12 h under vacuum. After the baking, the furnace was filled with 1 atm of
argon and heated to about 10°C above the melting temperature of GaSb (712°C). The synthesis was carried out by vertically raising and lowering the baffle in the melt for a period of 30–40 min (see Fig. 1). At the end of the synthesis cycle, the baffle was placed 1 cm away from the solid–liquid interface and the ampoule was lowered at a constant rate. During the solidification of the charge, the baffle either remained stationary or was rotated at the same axial elevation while the ampoule translated along the temperature gradient of the furnace. Forced convection in the melt was produced by (i) steady rotation of the baffle at 19 or 35 rpm, or (ii) oscillatory rotation, i.e., by alternating the direction of rotation while the baffle was rotated at 19 or 35 rpm. The frequency of alternating the direction of rotation was 0.37 s⁻¹. The furnace temperature gradient near the melt–solid interface was approximately 15 K/cm. The translation rate of the crucible was 3.3 mm/h in most of the experiments. In a few experiments, the translation rates were as high as 15 mm/h or as low as 2.5 mm/h. After solidification, the furnace was cooled down slowly to room temperature, over a period of several hours.

After the growth, the ingots were sliced parallel to the growth axis to evaluate the structural (Fig. 2) and compositional (Fig. 3) properties. To reveal the microscopic grain structures as shown in Fig. 2a–Fig. 2c and Fig. 2e, the following sequential chemical treatment was found suitable; HCl : 30% H₂O₂ : H₂O (1 : 1 : 1) followed by deionized (DI) H₂O dip and then CrO₃ (34.2 g) : HF (5 ml) : H₂O (120 ml) and H₂O dip and rinsing in soap solution. Compositions of the grown crystals (Ga, In, Sb) were evaluated by electron probe micro-analysis (EPMA) measurements in a JEOL 733 electron microprobe setup. The standards used were InSb and GaSb single-crystal substrates. Corrections for atomic number (Z), self-absorption (A) and fluorescence (F) effects (ZAF corrections) were performed by employing the commercial software SCOTT-I. Measured composition error was in the order of 1–2% of the measured values. The axial data presented in Fig. 3 are along the central line in the crystal.
Fig. 2. Longitudinally sliced and etched sections of In$_x$Ga$_{1-x}$Sb grown under different conditions: (a) $x = 0.03$, $v = 3.3$ mm/h, no baffle, (b) $x = 0.03$, $v = 3.3$ mm/h, stationary baffle, (c) $x = 0.03$, $v = 3.3$ mm/h, rotating baffle during first to freeze 0.5 fraction of the charge, (d) $x = 0.1$, $v = 3.3$ mm/h, oscillatory rotating baffle (unetched) and (e) $x = 0.1$, $v = 15$ mm/h, no baffle. The values of $x$ represent the InSb mole fraction in the melt.
3. Results and discussion

Preliminary experiments were performed with initial homogenized melts of $\text{In}_{0.03}\text{Ga}_{0.97}\text{Sb}$ to ascertain the role of the submerged baffle. Fig. 3a shows the axial indium distribution in a crystal grown without a baffle. The indium profile in the grown crystal clearly shows the dominance of convective conditions during growth, as expected for normal directional solidification [15]. The presence of a stationary baffle (see Fig. 3b) gives rise to an initial transient due to solute boundary layer build-up at the baffle bottom. However, as the indium concentration in the boundary layer rises, constitutional supercooling occurs and a sharp increase in the indium concentration is observed. This supercooling is repeated several times during the growth cycle, which leads to the observed wavy shape of the indium profile. Fig. 3c shows the indium profile in a crystal where the baffle was set to rotation at 35 rpm in the first-to-freeze 0.5 fraction of the melt and then kept stationary during the latter half. The rotation of the baffle (see Fig. 3c) gives the most homogeneous crystal. It can also be seen (Fig. 2c) that cracks appear in the crystal when the baffle rotation is stopped. The radial compositional homogeneity was also found to improve with the rotation of the baffle. Radial segregation in the first two cases (Fig. 2a and Fig. 2b) are similar. Even better results were obtained with an oscillatory rotation of the baffle than a steady rotation.

It is interesting to note that in spite of the absence of seed in these experiments, large single crystalline grain (>1 cm) are seen in Fig. 2a and Fig. 2b starting from the initial nucleation process. This may be due to wetting of the salt to the bottom of the ampoule, which avoids multiple nucleation by contact of semiconductor melt to the ampoule surface and slight asymmetric thermal conditions (to promote nucleation from the
corners. Additionally, lateral growth by competition between neighboring nucleus in the early growth stages coupled with a radial temperature gradient gives rise to such large grains. There is a one-to-one correlation between the grain structure along the longitudinal direction and the indium distribution (Fig. 2a, Fig. 3a, Fig. 2b and Fig. 3b). New grains appear when the indium concentration increases rapidly in the crystal. Such large grains (as in Fig. 2a and Fig. 2b) are not seen in Fig. 2c, where the baffle is rotated in the melt. This is probably due to the fact that by forced convection the melt temperature is highly uniform; thus, giving rise to equal probability of multiple nucleation. Lu et al. [29] also reported significant differences in grain structures with and without coupled vibrational stirring.

The growth experiment with oscillatory rotating baffle was further extended to the melt of In_{0.1}Ga_{0.9}Sb. Even though an oscillatory rotating baffle eliminates cracks, the grain size decreases with increasing InSb content in the melt. By lowering the rotation rate from 35 (Fig. 2c) to 19 rpm, the grain size could be enhanced without generating cracks in the crystals (Fig. 2d). This indicates that the oscillation rotation rate and frequency of the baffle need to be optimized for specific melt composition, melt size, and other growth parameters in order to eliminate cracks without diminishing grain size. The axial indium profile in this crystal (Fig. 3d) is similar to that in Fig. 3c. To enhance the grain size, tip nucleation was successfully employed in subsequent experiments.

A few solidification experiments were performed with growth rates of approximately 15 mm/h with the aim of obtaining axially homogeneous ingots. It is surprising to observe that such ingots do not exhibit any cracking. However, several inclusions were observed. There seems to be no effect of the baffle in these rapid solidification processes. The grain structure in ingots solidified with 10 mol% InSb in melt without and with a stationary baffle in the melt are similar (as depicted in Fig. 2e). The axial indium profile in these crystals are quite random due to the presence of inclusions; and, hence, inconclusive. The presence of the inclusions and possibly random super-cooled regions would limit the usability of these materials for device applications.

4. Conclusions

This present study demonstrates the significance of forced convection during the growth of mixed alloys (InGaSb in this case) that guarantees spatially homogeneous composition, otherwise unattainable even by post-growth thermal treatments. In turn, this inhibits cracking of the crystal and improves the microscopic crystalline quality.

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References