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**BULK CRYSTAL GROWTH OF ANTIMONIDE BASED III-V COMPOUNDS FOR
THERMOPHOTOVOLTAICS APPLICATIONS**

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Bulk crystal growth of antimonide based III-V compounds for TPV applications

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Abstract. In this paper, the bulk growth of crack-free GaInSb and single phase GaInAsSb alloys are presented. A new class of III-V quasi-binary $[A_{III}B_V]_{1-x}[C_{III}D_V]_x$ semiconductor alloys has been synthesized and bulk crystals grown from the melt for the first time. The present investigation is focused on the quasi-binary alloy $(GaSb)_{1-x}(InAs)_x$ ($0 < x < 0.05$) due to its importance for thermophotovoltaic applications. The structural properties of this melt-grown quasi-binary alloy are found to be significantly different from the conventional quaternary compound $Ge_{1-x}In_xAs_ySb_{1-y}$ with composition $x = y$. Synthesis and growth procedures are discussed. For the growth of ternary alloys, it was demonstrated that forced convection or mixing in the melt during directional solidification of $In_xGa_{1-x}Sb$ ($0 < x < 0.1$) significantly reduces cracks in the crystals.

INTRODUCTION

Semiconductor crystals with band gap in the range of 0.5 – 0.7 eV are needed for applications involving thermophotovoltaic (TPV) generation of electricity [1]. The availability of bulk substrates would significantly simplify the fabrication cycle, as the devices will be made on diffused junctions and the overall cost of the final device will be reduced. Although no elemental or binary semiconductor possesses such a band gap, this range of band gap can be realized in ternary alloys like $In_xGa_{1-x}Sb$, $In_xGa_{1-x}As$ and $InAs_yP_{1-y}$. The antimonide based system (InGaSb) is preferred over the arsenic and phosphorus counterparts due to technical simplicity during growth, like extremely low partial vapor pressure of antimony [2]. Usually, melt-grown InGaSb crystals exhibit a high density of cracks due to: (1) large lattice mismatch between InSb and GaSb, and (2) segregation of InSb during growth due to the large separation between the liquidus and solidus curves in the pseudo-binary phase diagram of the GaSb-InSb system [3]. These features make the growth of single crystals of ternary alloys from melt extremely difficult. The lattice mismatch also hinders the use of binary seeds like GaSb, InAs, or InSb for single crystal growth. Therefore, ternary semiconductor crystals are currently produced in the form of thin layers ("epitaxy" or

thin film growth) by non-equilibrium growth techniques (from diluted solutions and vapor phase) on binary substrates using compositionally graded buffer layers to reduce the stress in the mismatched lattice. Lattice matching to GaSb or InAs can be achieved by incorporating arsenic to form GaInAsSb quaternary alloys. Miscibility gaps in the pseudo-quaternary systems and phase separation are the main obstacles for quaternary alloy solidification from melts [4,5]. These arise mainly from differences in chemical interactions between the constituent elements in the melt. Therefore, quaternary semiconductor crystals are also produced in the form of thin layers by non-equilibrium epitaxial growth techniques either from diluted solutions or vapor phase. In this paper, we addressed the issues of crack elimination during the bulk growth of $_{1-x}^{Ga}In_xSb$ and avoiding multiphase formation during the growth of GaInAsSb quaternary alloys. It was demonstrated that forced convection or mixing in the melt during directional solidification of bulk $In_xGa_{1-x}Sb$ ($0 < x < 0.1$) ternary alloys significantly reduces cracks in the crystals. Growth of single phase GaInAsSb quaternary alloys has been demonstrated from chemically associated melt [6].

EXPERIMENTAL DETAILS

Growth of GaInSb

Synthesis of $In_xGa_{1-x}Sb$ has been carried out in a multi-zone Mellen furnace [7] in 32 mm diameter silica crucibles from pre-synthesized GaSb and InSb freshly etched with CP4 etchant ($CH_3COOII : HF : HNO_3$ 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. A pre-growth baking of the charge and salt (to remove moisture) was carried out at approximately 300°C for a period of 10 - 12 hours 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 minutes. 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. Forced convection in the melt [8] was produced by (1) steady rotation of the baffle at 19 or 35 rpm, or (2) 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 $15\text{ }^{\circ}\text{C/cm}$. The translation rate of the crucible was 3.3 mm/hr. After solidification, the furnace was cooled down slowly to room temperature, over a period of several hours.

Growth of GaInAsSb

The quaternary GaInAsSb alloys were synthesized from various combinations of starting elements (Ga, In, Sb) and compounded (InAs, GaSb, GaAs, InSb). Synthesis was carried out in a multi-zone Mellen furnace (vertical Bridgman set-up) in 20 and 32 mm diameter silica. Melt encapsulation was provided by boric oxide (B_2O_3) or alkali halide salts (LiCl-KCl and NaCl-KCl). Boric oxide encapsulation was found to be more satisfactory and suitable (due to extremely low vapor pressure and high viscosity) for inhibiting volatilization from the melt surface. The growth chamber was usually pressurized to slightly more than 1 atm by argon gas to prevent decomposition of the arsenic based compounds. Synthesis was done at various temperatures in the range of $712 - 945\text{ }^{\circ}\text{C}$. After synthesis, the crucible was lowered at a constant rate of 3.3 mm/hr through a temperature of $15 - 20\text{ }^{\circ}\text{C/cm}$. At the end of solidification, the furnace was cooled down slowly to room temperature over a period of several hours. Crystal growth was performed without seed, either in flat bottom or conical tipped crucibles.

After the growth, the ingots (GaInSb and GaInAsSb) were sliced parallel to the growth axis to evaluate the structural and compositional properties. The composition of the grown crystals (Ga, In, Sb, and As) was evaluated by the Electron Probe Micro-Analysis (EPMA) measurements in a JEOL 733 electron microprobe set-up. The standards used were InAs, InSb, GaAs 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. The error in determining the composition was in the order of 1-2% of the measured values. The microstructures of the crystals were studied through Secondary Electron Microscopy (SEM) in the EPMA set-up.

RESULTS AND DISCUSSION

Crack elimination in GaInSb

Fig. 1a shows a typical GaInSb crystal grown from a melt containing 5 mol% InSb - 95 mol% GaSb without a baffle in the melt. Cracks typical of ternary alloys are clearly seen in this crystal. Fig. 1b shows a typical crystal grown from a melt of 10 mol% InSb - 90 mol% GaSb with a rotating baffle. Unlike the crystal in Fig. 1a, no cracks could be seen in this crystal. Moreover, the rotating baffle significantly improves the axial and radial compositional homogeneity in the grown crystal.

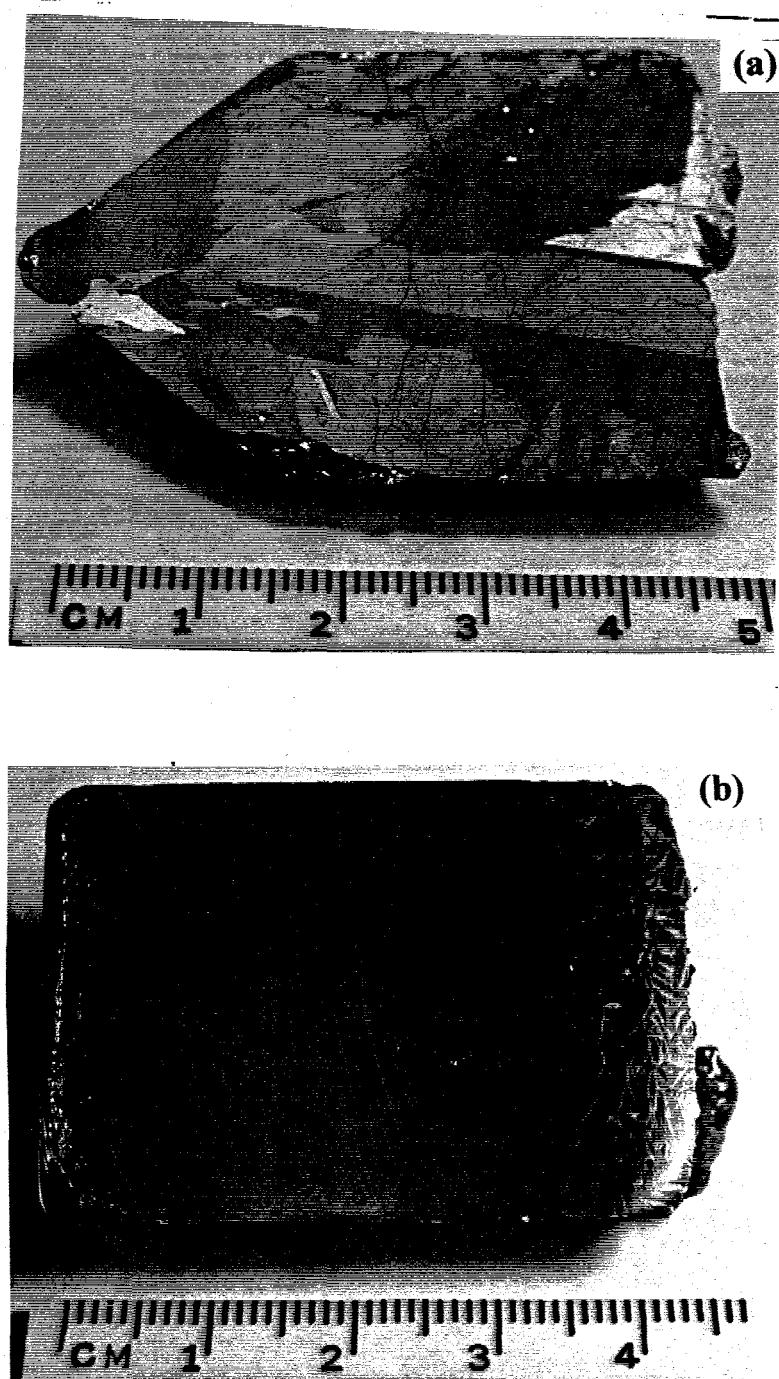


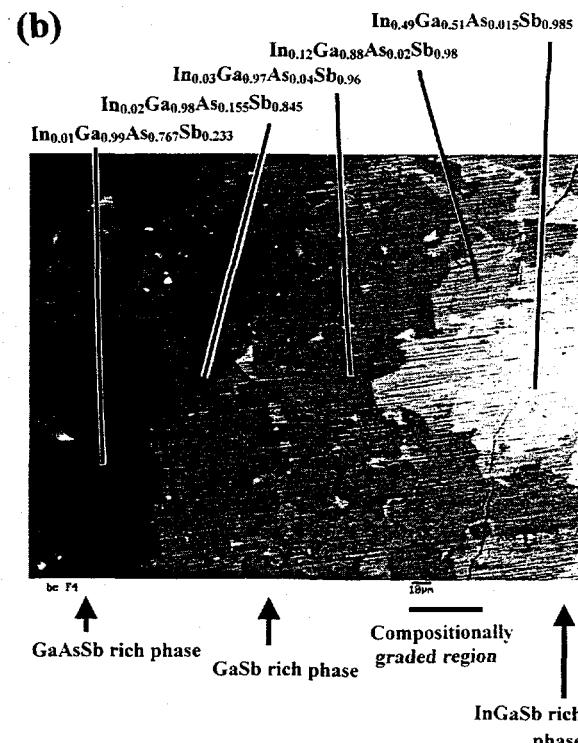
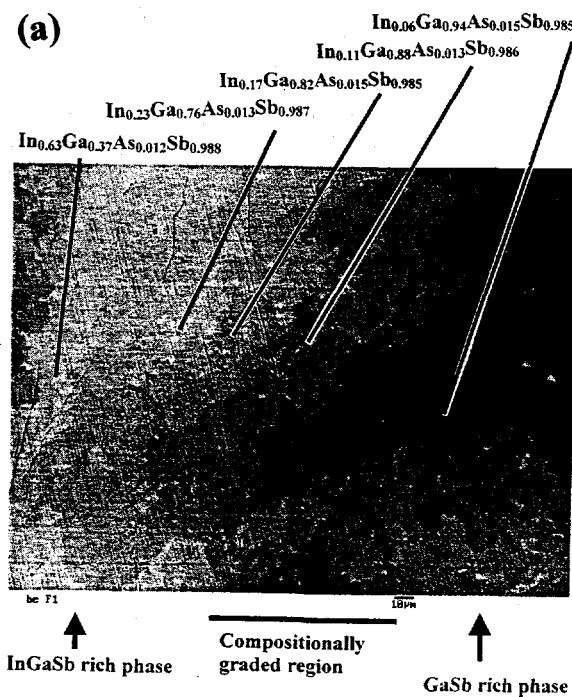
FIGURE 1. Longitudinally sliced $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ crystals grown (a) without a baffle; $x = 0.05$, $v = 3.3$ mm/hr, (b) with a rotating baffle; $x = 0.1$, $v = 3.3$ mm/hr.

Growth of single phase quaternary or quasi-binary alloys

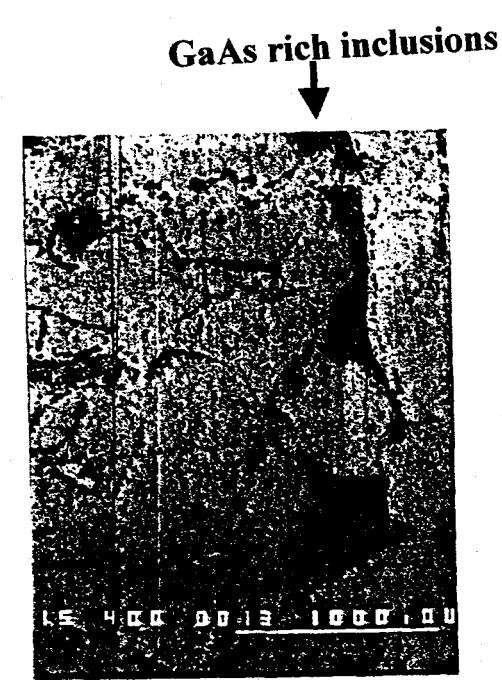
In the absence of any phase diagrams, the initial studies were focused towards studying the microstructure of quaternary

$_{1-x} \text{In}_x \text{As}_y \text{Sb}_{1-y}$ synthesized at various temperatures and charge preparation cycles from melts containing 20 mol% In, 80 mol% Ga, 13 mol% As, and 87 mol% Sb. This alloy composition was attempted with the aim of obtaining a band gap of ~ 0.55 eV which is necessary for specific TPV applications. In preliminary studies, spatial inhomogeneity in the crystal composition due to the multi-phase formation was observed as shown in Fig. 2(a-c). Phase separation is thermodynamically expected in quaternary systems grown from a regular solution [4]. The multi-phase formation is attributed to the presence of elemental sources.

Fig. 2a shows the microstructure of $_{1-x} \text{In}_x \text{As}_y \text{Sb}_{1-y}$ synthesized at 950°C from melt containing elemental Ga, In, Sb, and compounded InAs (arsenic source).



The multiple phases are formed due to the decomposition of InAs and subsequent formation of random mixed alloys with elemental Ga, In, and Sb. Fig. 2b shows typical microscopic phases observed in $_{1-x}^{Ga}In_xAs_ySb_{1-y}$ synthesized from a melt containing elemental Ga, In, Sb, and compounded GaAs (arsenic source) at 950°C. Low synthesis temperature improves the compositional homogeneity. However, it does not fully avoid the formation of multiple phases. Fig. 2c shows inclusions in the quaternary crystals synthesized at 800°C from the same melt composition as the crystal in Fig. 2b. By correlating the microstructure of the crystals with the melt constituents, it can be concluded that the multiple phase formation arises from chemical interaction between elemental sources in the melt. Hence, they can be suppressed by synthesizing the charge from compounded sources as discussed below.



(c)

FIGURE 2. Microstructures (SEM photomicrograph) of $_{1-x}^{Ga}In_xAs_ySb_{1-y}$ quaternary alloys synthesized from (a) Ga, In, Sb and InAs at 950°C, (b) Ga, In, Sb and GaAs at 950°C, (c) Ga, In, Sb and GaAs at 800°C. The mol % for In, Ga, As, and Sb in the melt were 20, 80, 13, and 87, respectively.

Typical microstructure of the quasi-binary $(GaSb)_{1-x}(InAs)_x$ synthesized in the 720 – 850°C temperature range from compounded GaSb and InAs is depicted in Fig. 3a [6]. From SEM studies, it is concluded that the quasi-binary crystals are completely single phase in nature, unlike the quaternary alloys. Moreover, synthesis from compounded sources significantly reduces the probability of multi-phase formation. It is also evident from the comparison of Figs. 3a and 3b, that the quasi-binary GaSb-InAs crystals do not exhibit cracks, unlike their ternary GaSb-InSb counterpart. This is due to 10 times less lattice mismatch of InAs and GaSb as compared to InSb and GaSb.

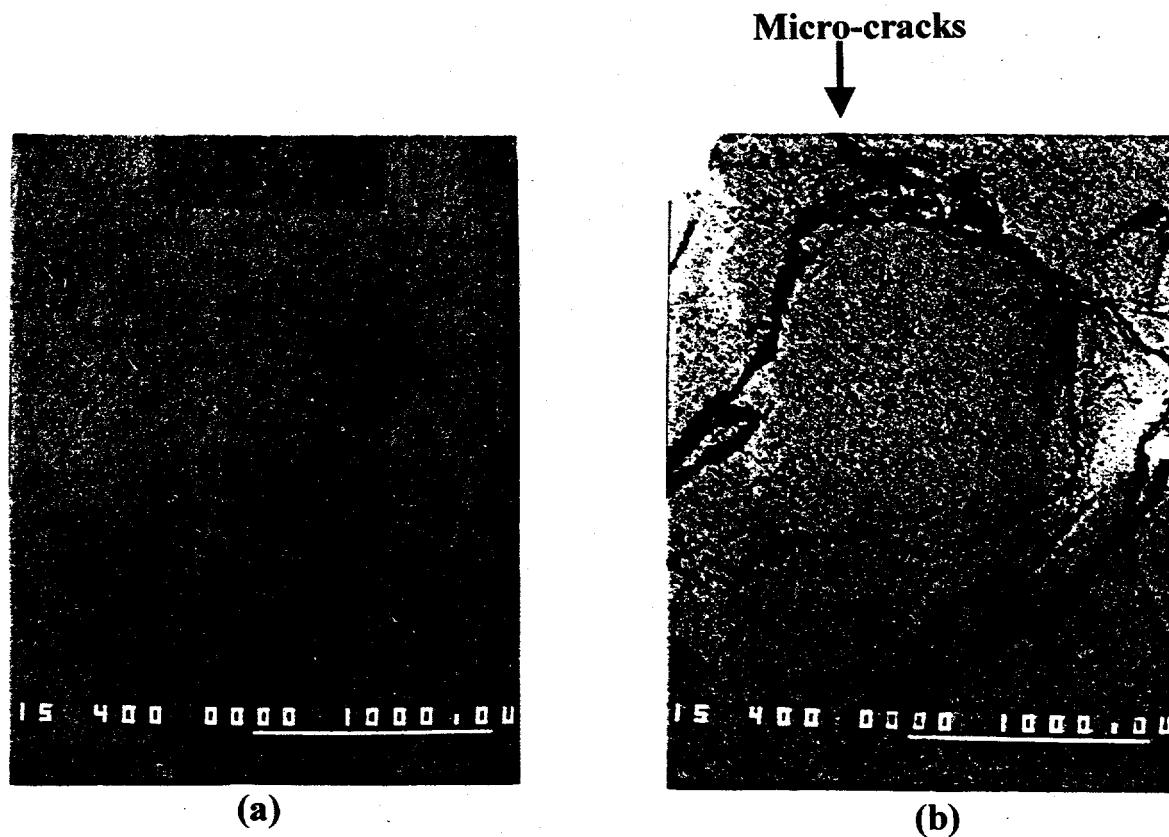


FIGURE 3. Microstructures (SEM photomicrograph) of (a) $(\text{GaSb})_{0.97}-(\text{InAs})_{0.03}$ quasi-binary alloy synthesized from GaSb and InAs, (b) $(\text{GaSb})_{0.97}-(\text{InSb})_{0.03}$ ternary alloy synthesized from GaSb and InSb

CONCLUSION

In conclusion, the present study demonstrates that the use of forced convection during the growth of mixed alloys (InGaSb in this case) will produce spatially homogeneous composition, otherwise unattainable even by post growth thermal treatments. In turn, homogeneous composition inhibits cracking of the crystal and improves the microscopic crystalline quality. Large polycrystals of semiconductor quasi-binary alloys of $(\text{GaSb})_{1-x}-(\text{InAs})_x$ were grown from melt for the first time. These alloys possess better crystalline perfection (crack free and are single phase) and compositional homogeneity (close to unity segregation) than melt grown bulk ternary and quaternary alloys.

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