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BRIDGMAN GROWTH AND CHARACTERIZATION OF BULK SINGLE CRYSTALS OF $Ga_{1-x}In_xSb$ FOR TPV APPLICATIONS

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BRIDGMAN GROWTH AND CHARACTERIZATION OF BULK SINGLE CRYSTALS OF $Ga_{1-x}In_xSb$ FOR THERMOPHOTOVOLTAIC APPLICATIONS

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ABSTRACT

Thermophotovoltaic generation of electricity is attracting renewed attention due to recent advances in low bandgap (0.5-0.7 eV) III-V semiconductors. The use of mixed pseudo-binary compounds allows for the tailoring of the lattice parameter and the bandgap of the material. Conventional deposition techniques (i.e., epitaxy) for producing such ternary or quaternary materials are typically slow and expensive. Production of bulk single crystals of ternary materials, for example $Ga_{1-x}In_xSb$, is expected to dramatically reduce such material costs. Bulk single crystals of $Ga_{1-x}In_xSb$ have been prepared using a Bridgman technique in a two-zone furnace. These crystals are 19 mm in diameter by approximately 50 mm long and were produced using seeds of the same diameter. The effects of growth rate and starting materials on the composition and quality of these crystals will be discussed and compared with other attempts to produce single crystals of this material.

INTRODUCTION

III-V compound semiconductors are important materials for optoelectronic applications, in particular for thermophotovoltaic generation of electricity [1]. By alloying different compounds, the bandgap and the lattice parameter of the resulting combination can be adjusted. Tailoring these properties allows for the fabrication of a wider array of devices than is possible using only the simple binary materials. One of the many possible combinations currently receiving significant attention is the GaSb-InSb system. Combinations of these compounds can have lattice constants in the range of 0.6096 to 0.6479 nm and bandgaps between 0.17 and 0.726 eV [2].

Typical deposition techniques, such as liquid phase epitaxy, are expensive for fabricating these materials. The ability to grow large, bulk single crystals of these materials is expected to reduce their cost. For this to be effective, however, the composition of the alloy material must be uniform over a significant portion of the resulting boule. This is difficult to achieve for most compound semiconductor materials because of the wide and non-uniform liquidus-solidus separation of the pseudo-binary phase diagram. Additionally, as with the growth of crystals of most materials, solute transport and temperature variation within the melt also have important effects on the composition and quality of the final material produced. Previous work to produce GaSb-InSb alloys via different techniques and conditions is reported in [3] - [7].

In this paper, results of some experiments conducted to prepare bulk alloys of $Ga_{1-x}In_xSb$ (x~0.03 and 0.2) and to explore the effects of growth parameters on the composition of the resulting alloy are presented. A Bridgman technique was used to solidify the melt; single crystal and polycrystalline boules were produced. Seeds of the same diameter as the crucible were used to grow single crystals of the alloy to reduce the likelihood of twinning and other defects.

EXPERIMENT

Preparation of Binary Starting Compounds

The binary compounds, GaSb and InSb, were prepared in the laboratory. The starting materials were elements with 6N purity. In both cases, the Sb-III atom ratio was ~1.001 to allow for volatilization of Sb during processing. A fused silica crucible, with an inner diameter of 19 mm and an overall length of approximately 125 mm, was used to contain the mixture. The crucible was cleaned with HF, followed by rinses of deionized water and isopropanol, then dried with filtered argon. The starting materials, without any etching or cleaning, were placed into the cleaned crucible, then inserted into the furnace.

A two-zone transparent furnace (Trans-Temp, Chelsea, MA) was used for all experiments (Figure 1). The crucible was held in a graphite support (Figure 2a). A quartz rod, prepared in the same way as the crucible, was inserted from the top for use in mixing the melt.

After the crucible was inserted, the furnace was evacuated to ~100 millitorr, then flushed with argon (three cycles). An argon flow of ~1 slpm was maintained during furnace operation.

For GaSb synthesis, the hot zone and cold zone temperatures were 780 C and 600 C, respectively; for InSb synthesis, the hot zone and cold zone temperatures were 750 C and 450 C, respectively. The Type S control thermocouples were located in each zone such that a thermal gradient zone of *G*~25 K/cm was established in the middle portion of the furnace. The crucible

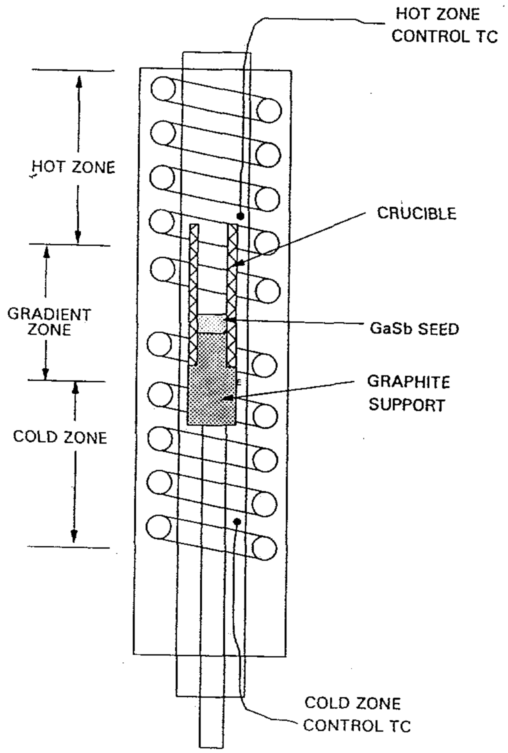

Fig. 1. Schematic of two-zone transparent furnace. The inner diameter of the inner quartz tube is 32 mm; the inner diameter of the gold-coated outer tube is 80 mm. Overall heated length is 60 cm.

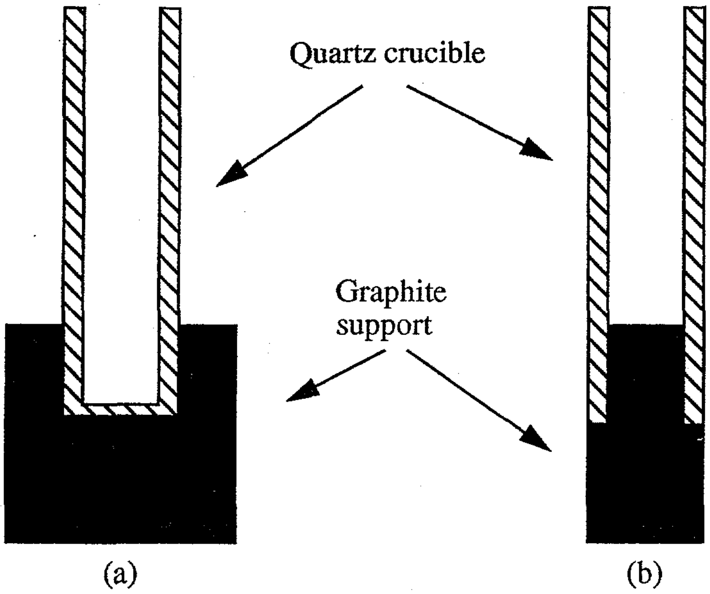

Fig. 2. Schematic of crucible and graphite supports used for synthesis and crystal growth. (a) Flat-bottomed crucible for binary compound synthesis and polycrystalline alloy fabrication. (b) Open tube crucible for single crystal growth.

was positioned within the furnace such that the support temperature was above the melting point of the compound being synthesized (712 C for GaSb and 535 C for InSb). After the charge material was completely melted, the quartz rod was used to mix the melt. Mixing was done every 45 to 60 minutes during the synthesis. After 4 to 5 hours, the crucible was pulled into the cold zone at a rate of 7 mm/hr, then the furnace was slowly cooled to room temperature in stages.

The polycrystalline boules were removed from the crucible, sectioned using a diamond saw, then characterized by electron microprobe and X-ray diffraction.

Synthesis of Polycrystalline $Ga_{1-x}In_xSb$ Boules

Polycrystalline $Ga_{1-x}In_xSb$ boules were made using flat bottomed crucibles without seeds. Starting materials were either the binary compounds or the three elements (6N purity) in appropriate ratios to achieve initial melt compositions of x~3 or x~20. When the elements were used, the Sb-III ratio was ~1.001; material and crucible preparation, melt mixing, and homogenization were performed in the same manner as described for the binary synthesis experiments. When the starting materials were the binary compounds, the same processes as described below for single crystal growth were used. The crucible translation rate, v, for these experiments ranged from 3 to 19 mm/hr. Furnace preparation and operation were the same as described for single crystal growth experiments.

Growth of Single Crystals of $Ga_{1-x}In_xSb$

Single crystals of $Ga_{1-x}In_xSb$ were grown in a quartz crucible supported by a graphite plug (Fig. 2b). Starting materials were GaSb and InSb in amounts to achieve an initial melt composition,

x, of approximately 0.03. A 19 mm diameter by 10 mm thick <111> GaSb seed (Atramet, Inc., Hempstead, NY) was used. The crucible and a quartz rod were prepared in the same manner as that used for compound synthesis, while the graphite plug was rinsed with isopropanol and dried with filtered argon. The compounds and the seed were etched in modified CP-4 etchant ($5\,HNO_3 : 3\,HF : 3\,HAc : 11\,H_2O$), then rinsed with deionized water and isopropanol. The seed was dried with filtered argon and inserted into the crucible with the (111)B (Sb) face oriented toward the melt. The furnace was evacuated and flushed with argon as previously described; argon flow at ~1 slpm was maintained during growth and cooldown. The cold zone and hot zone temperatures were maintained at 600 C and 780 C, respectively; the crucible was located within the gradient zone of the furnace such that the support thermocouple indicated approximately 690 C. After the charge was melted, it was mixed using the quartz rod, allowed to homogenize for up to one hour, and then remixed. The crucible was repositioned until the top of the seed was observed to melt. The melt was remixed, then allowed to equilibrate for about 20 minutes prior to initiating solidification. The crucible was pulled toward the cold zone at rates of 3 to 7 mm/hr. After solidification was completed, the furnace was gradually cooled to room temperature in stages. The crucible was removed from the furnace and the boule was sectioned for characterization.

RESULTS AND DISCUSSION

All of the GaSb and InSb boules were sectioned longitudinally and etched using modified CP-4 etchant. The boules were polycrystalline, with elongated grains oriented with their major axis parallel to the solidification direction. Electron microprobe analysis (EMPA) indicated that each boule had a III-Sb ratio of 1:1 within analytical error. X-ray analysis produced diffraction patterns consistent with standard patterns for the respective compounds. Figure 3 shows a photograph of a typical GaSb boule.

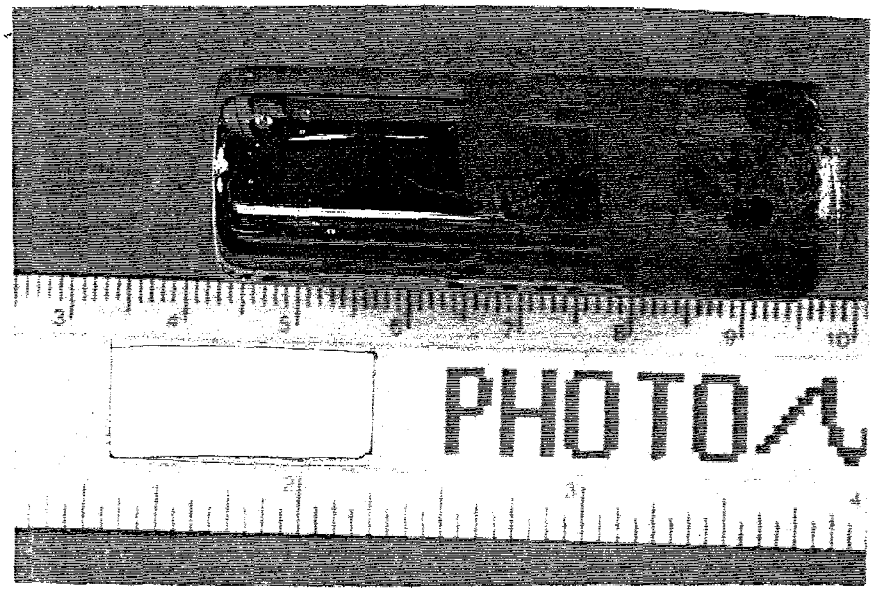

Fig. 3. Typical GaSb boule as removed from the crucible.

Figures 4 and 5 illustrate the longitudinal variation in composition for two polycrystalline boules grown at 19 mm/hr with elemental starting materials in different initial compositions. The former had an initial composition of x=0.03, while the latter was initially at x=0.2. Figure 6 shows the axial chemical composition of a polycrystalline boule grown from a melt of the binary compounds at 19 mm/hr with an initial melt composition of x=0.03. In all cases, the boules grown from a melt with lower x produced a more uniform composition along the boule compared with that produced from the higher melt fraction. Some constitutional supercooling

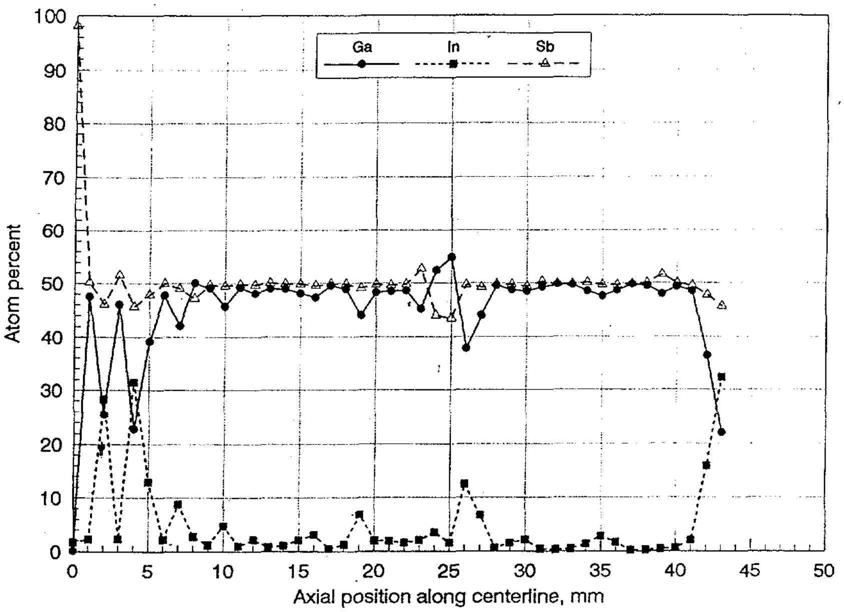

Fig. 4. EMPA measurements of chemical composition along the centerline of a polycrystalline $Ga_{1-x}In_xSb$ boule. The starting materials were elements with an initial composition of x=0.03; the solidification rate was 19 mm/hr.

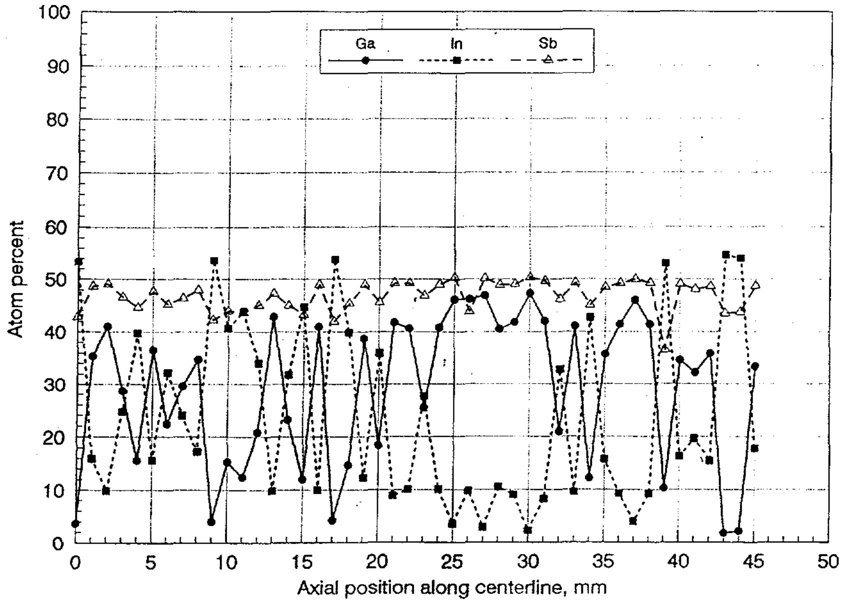

Fig. 5. EMPA measurements of chemical composition along the centerline of a polycrystalline $Ga_{1-x}In_xSb$ boule. The starting materials were elements with an initial composition of x=0.2; the solidification rate was 19 mm/hr.

may have occurred in the former boules, although it was not as significant as that observed in the boule produced from the less dilute melt. Additionally, the boule grown from the binary compounds did not exhibit high indium levels in the first-to-freeze portion, unlike those found in the boule grown from a melt of equivalent x produced from the elements.

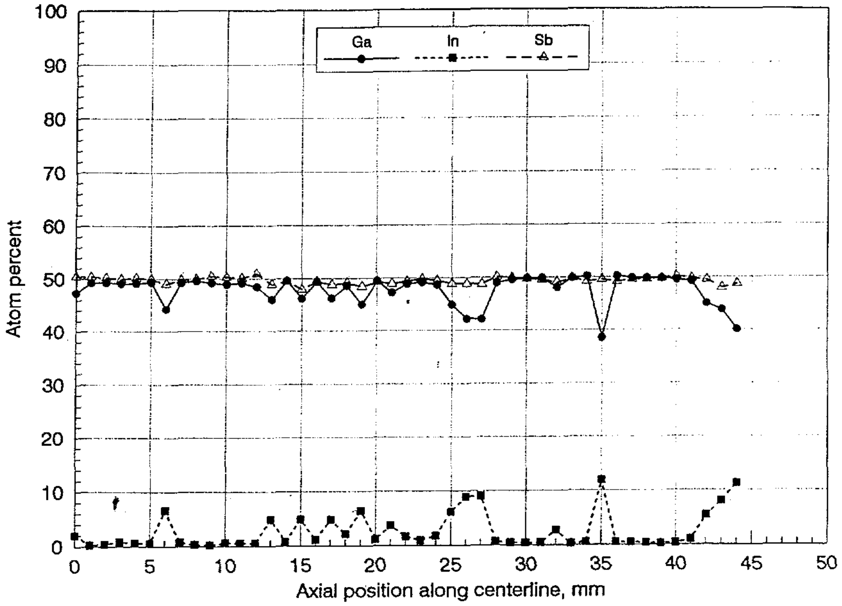

Fig. 6. EMPA measurements of chemical composition along the centerline of a polycrystalline $Ga_{1-x}In_xSb$ boule. Starting materials were GaSb and InSb with an initial composition of x=0.03; solidification rate was 19 mm/hr.

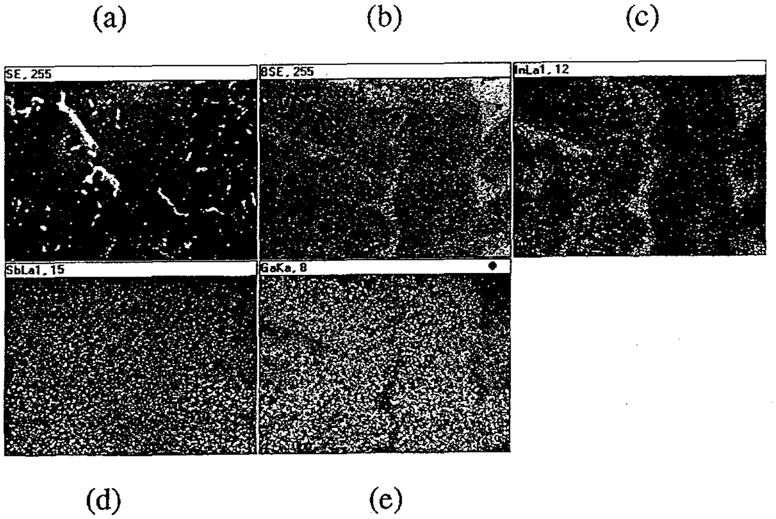

Fig. 7. Elemental maps of a polycrystalline $Ga_{1-x}In_xSb$ boule produced from the elements with an initial composition of x=0.03 at a solidification rate of 19 mm/hr. 30X magnification. (a) Secondary electron image. (b) Backscattered electron image. (c) Indium map. (d) Antimony map. (e) Gallium map.

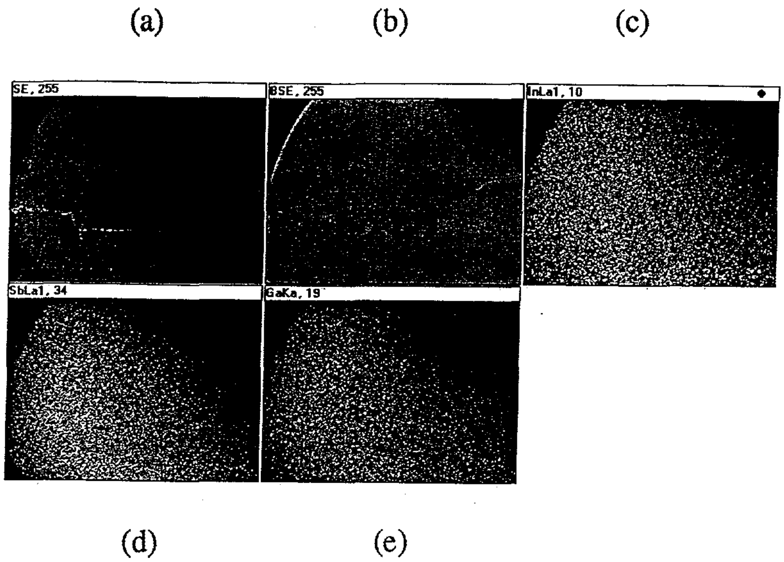

Fig. 8. Elemental maps of a polycrystalline $Ga_{1-x}In_xSb$ boule produced from GaSb and InSb with an initial composition of x=0.03 at a solidification rate of 19 mm/hr. 30X magnification. (a) Secondary electron image. (b) Backscattered electron image. (c) Indium map. (d) Antimony map. (e) Gallium map.

Elemental maps of the polished surfaces of each boule were made using a scanning electron microscope. Boules grown from elemental starting materials were found to have localized segregation of the elements throughout the boule, as illustrated in Figure 7. No sharp compositional changes were noted across any of the cracks in these boules. When the binary compounds were used as the starting materials, no elemental segregation was observed (Fig. 8) except in the last-to-freeze region.

The formation of elemental clusters in the alloy boules grown rapidly from elemental starting materials is in contrast to the uniform local elemental distributions found in the binary compounds grown under similar conditions. The presence of the third atom appears to have a pronounced effect on the diffusion and reaction rates within the melt. The rapid solidification rate exacerbated this effect by producing a locally varying composition before equalization of the composition could occur. This is similar to results reported in [5], in which it was determined that zone melting would produce equilibrium solid solutions only at zone translation rates of less than 3 mm/hr.

Figure 9 shows a single crystal of $Ga_{1-x}In_xSb$ (x=0.03) grown at 7 mm/hr. Although no grain boundaries are present, several twins were formed; all of these appear to have initiated at the crucible wall. Cracks were observed throughout the sectioned boule. X-ray diffraction confirmed uniform crystal orientation along the length of the boule. The results of EMPA measurements are shown in Figure 10. The predicted composition variation based on the Pfann distribution for normal freezing [8] is also shown in Figure 10. This curve was calculated using a constant segregation coefficient, k, of 0.22, which was obtained from the pseudo-binary phase diagram [9] at the initial melt composition. This growth resulted in significant compositional variation due to constitutional supercooling.

A boule of $Ga_{1-x}In_xSb$ (x=0.03) grown at 3 mm/hr at identical conditions is shown in Figure 11. The first 75% of this boule is a single crystal with some twin boundaries which again initiated at the cruible wall; near the end of the growth of this boule, multiple grains and twins were formed. Small cracks were found only in the upper quarter of this boule. The axial InSb composition is shown in Figure 12.

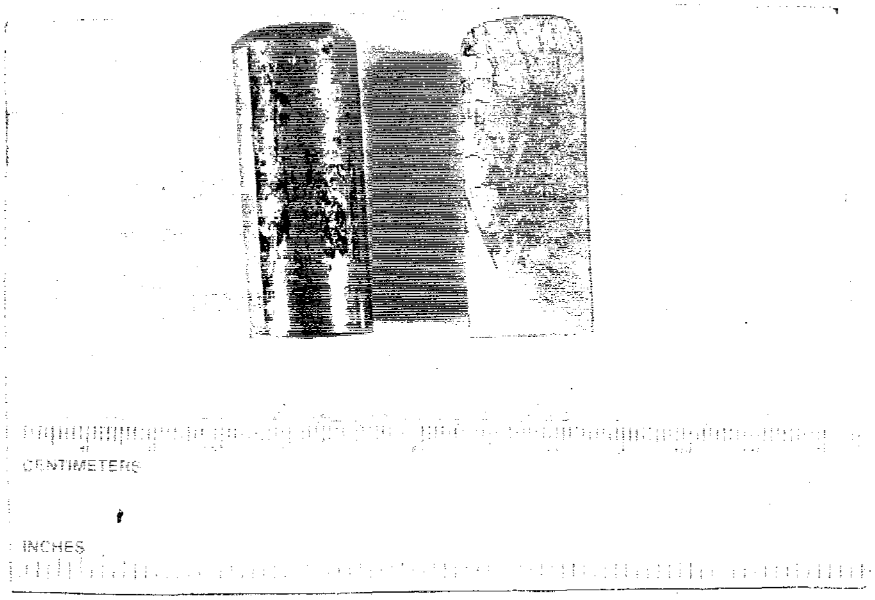

Fig. 9. Single crystal of $Ga_{1-x}In_xSb$ grown at 7 mm/hr. The initial melt composition was x=0.03. A (111) GaSb single crystal seed with the B face toward the melt was used.

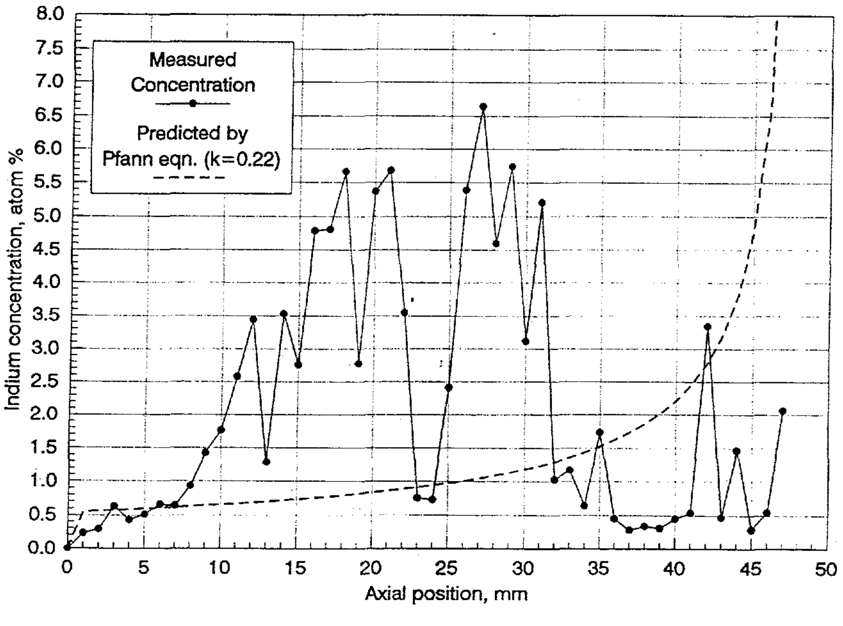

Fig. 10. Axial indium distribution in the single crystal shown in Fig. 9 as measured by EMPA. The indium composition predicted by the Pfann equation [8] for k=0.22 is shown for comparison.

The change in InSb composition in the more slowly grown boule is consistent with stable directional crystal growth from a well-mixed melt with a variable *k*. In these experiments, mixing of the melt resulted from natural convection. The variation in *k* as solidification progressed is consistent with that measured and tabulated for Czochralski growth of this alloy [7], and is due to

Fig. 11. Single crystal of $Ga_{1-x}In_xSb$ grown at 3 mm/hr. The starting materials were GaSb and InSb with an initial melt composition of x=0.03. A (111) GaSb single crystal seed with the B face toward the melt was used.

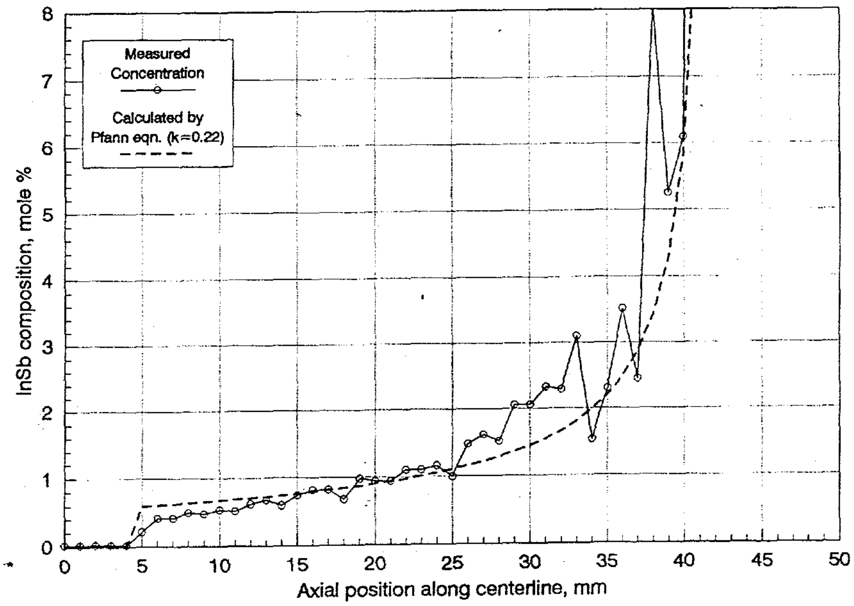

Fig. 12. Axial indium distribution in the single crystal shown in Fig. 11 as measured by EMPA. The indium composition predicted by the Pfann equation [8] for k=0.22 is shown for comparison.

the increasing separation between the liquidus and solidus as the fraction of InSb increases in the melt. These results show that constitutional supercooling of this alloy can be avoided if the ratio *G/v* is greater than about 8 K-hr/cm^2. This is well below the value of 260 K-hr/cm^2 determined by Yee, et al. [6], for $Ga_{1-x}In_xSb$ ($0.1 \leq x \leq 0.5$) grown in space by a gradient freeze technique. The lower critical value of *G/v* indicates that significantly lower thermal gradients and faster growth rates than those expected from previous works can be used to produce large bulk single crystals of dilute $Ga_{1-x}In_xSb$ alloys.

The cracking observed in the boule grown at 3 mm/hr (Fig. 11) occurred in the last-to-freeze region where the composition is changing most rapidly. The large variations in composition and the presence of cracks throughout the boule grown at 7 mm/hr (Fig. 9) are consistent with this observation. These observations suggest that large compositional gradients may be producing lattice strain and cracks in the boules. It should be noted that Bachmann, et al. [7], suggested that Czochralski growth of $Ga_{1-x}In_xSb$ up to x~0.4 could be done without misfit strain in the neck resulting in cracking in the crystal neck. Additionally, Yee, et al. [6] observed that the tendency of these alloys to develop microcracks increased with increasing InSb content. These results support the conclusions of Bachmann, et al. [7], that growth of $Ga_{1-x}In_xSb$ alloys with high x will require a stepwise approach, using gradually increasing levels of InSb in the seed crystals and in the melts.

CONCLUSIONS

Bridgman growth of single crystals of dilute $Ga_{1-x}In_xSb$ alloys was shown to be feasible for *G/v* ratios in excess of ~8 K-hr/cm^2. The use of seed crystals of the same diameter as the growth crucible has also been shown to be an effective means of growing these crystals. Local compositional variations in the ternary alloys can be avoided if the starting materials are the binary constituents instead of the high purity elements. This may be due to reduced diffusion and reaction rates within the ternary melt compared with those that occur in binary melts. The combination of high growth rates and binary compound starting materials results in a reasonably uniform axial composition in polycrystalline $Ga_{1-x}In_xSb$ boules. Lastly, the ability to grow bulk single crystals of dilute $Ga_{1-x}In_xSb$ alloys without cracking is dependent upon the ability to control the variation in InSb composition on a macroscopic scale.

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