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Indium segregation in bulk GaInSb crystal grown using vibration assisted vertical directional solidification technique

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Abstract

Bulk crystals of $Ga_{0.9}In_{0.1}Sb$ have been grown using vertical directional solidification (VDS) technique. The experiments were carried out using resistive furnace with temperature gradient of 10 ^{0}C/cm. The 4N grade Gallium (Ga) Indium (In) and Antimony (Sb) were taken in stoichiometric proportion and sealed in a quartz ampoule with cone angle 30^o, under Argon atmosphere at pressure of 100 Torr. The compositional analysis has been done using EDAX technique. The effects of external vibrations on significant improvement in segregation of Indium content, associated multiphase growth and microcracks in crystal has been discussed.

Keywords: GaInSb, Indium segregation.

Introduction

GaInSb is a narrow band gap III-V ternary alloy semiconductor having advantage of tuneable lattice parameter and band-gap ranging 6.096 A^o to 6.479A^o and 0.73 eV to 0.17 eV respectively by adjusting its relative composition of Gallium and Indium [1-5]. This particular regime of band-gap is promising for lasers, photodetectors and thermophotovoltaic applications in infrared spectrum. However, due to difference in atomic radii of substituting Ga and In atoms, convection flows in liquid and large solidius-liquidus separation in GaSb-InSb phase diagram, it is difficult to grow high-quality InGaSb alloy bulk crystals using classical bulk melt growth techniques [6,7,8]. The segregation of In and convection flows in liquid due to temperature gradient results into polycrystalline crystal [9,10]. To improve the crystalline quality of this material, many efforts such as accelerated crucible rotation technique [10], growing crystals in space with microgravity [12], controlled solute feeding [13], vibrations [14] and alternating magnetic field [15] were made for past two-three decades. However, due to inherent problems in growing them from melt, bulk single crystal substrates of ternary semiconductors are still not available for commercial applications.

The present study focuses on effect of controlled mechanical vibrations on bulk crystal growth of $Ga_{0.9}$ $In_{0.1}Sb$ alloy using indigenously fabricated synthesis unit of vertical directional solidification (VDS) technique [16]. Two experiments, one without vibration and other with vibrations, have been carried out by keeping all other growth parameter constant. The grown crystals have been characterized using energy dispersive X-ray (EDAX) analysis, metallurgical microscope and XRD analysis. It has been demonstrated that controlled mechanical vibrations enhance the mixing of Indium accumulated at solid –liquid interface and improve chemical homogeneity in GaInSb crystal growth using VDS technique.

Methodology

For synthesis of $Ga_{0.9}$ $In_{0.1}Sb$, granules of 4N grade (Manufacturer: Alpha Aesar , US) Gallium (Ga) Indium(In) and Antimony (Sb) were taken in stoichiometric proportion and sealed in a quartz ampoule (length = 10 cm, inner diameter = 14 mm, cone angle = 30^o) under Argon pressure of 100 Torr. To avoid the oxidation due to ampoule cracking during growth process, the ampoules containing starting material were sealed in another quartz ampoule under Argon at normal pressure. The vertical temperature gradient of furnace between the temperature from 730 ^{0}C to 500 ^{0}C was set to10 ^{o}C/cm. To achieve homogenous mixing, sealed ampoule was kept at 800^{0}C for 10 hours with continuous mechanical vibrations of 50 Hz and maximum amplitude 0.35 mm. After 10-hour mixing, tip of ampoule was lowered to melting temperature of GaSb for self-seed formation and kept at this temperature for 10 hours for nucleation. After 20 hours, the ampoule lowering rate was kept 1 mm/hour with continuous axial mechanical vibrations of frequency ranging from 50 Hz to 150 Hz and vibration amplitude of 0.25 mm. To avoid the localized resonance vibrations and destabilization of interface, vibration frequency was varied from 50 Hz to 100 Hz, with continuous repetition cycle of 30 seconds. The schematic of VDS system and ampoule lowering profile are shown in fig.1 and fig. 2 respectively. To remove lattice misfit strains due to compositional inhomogeneity, ingot was annealed at 400 ^{0}C for 10 hours.

The ampoule stecking to ingot was not observed in both with and without vibration experiments. However, ampoule cracking was observed in both with and without vibration ecperiments (fig.3). The as grown ingots (fig.4) were sliced perpendicular to axis by using low speed diamond coated crystal cutter and polished using alumina abrasive powder of 1 µm size to get mirror finish surface.

Characterization

1. Spatial distribution of constituent elements:

The axial and radial compositional analysis was carried out using EDAX (Model: FEI Quanta 200 ESEM system) with instrumental error of ± 0.1 atomic percentage (Fig.5). From graphs of composition variations in case of with vibration (fig.6) in conical region of ingot, Indium atomic percentage increases gradually from 6.6% to 11.8%. In cylindrical region of constant diameter, it gradually decreases from 11.8 % to 9.5%. From graphs of composition variations in case of without vibration (fig.7), Indium concertation increases continuously. Also, in both with and without vibration experiment, the radial composition variation is of the order of 0.3 and 0.5 atomic percent respectively.

2. Microstructure Analysis:

For microstructure analysis, wafers of 0.7 mm thickness were mirror polished by 0.5 µm size alumina abrasive powder and etched by selective chemical etchant (HNO_3: HF:CH_3COOH: H_2O: 3:3:2:15 by volume percentage). The developed patterns were analyzed by metallurgical microscope with CCD camera attachment. Relatively large grains, as shown in fig.8, are found in growth with vibrations. Also, relatively more numbers of microcracks, as shown in fig.9, are observed in growth without vibrations. The triangular itch pit pattern, as shown in fig.10, revels the oriented growth along (111) plane. In case of growth with vibration, number of grain boundaries decreases, while twin lamellae were increased. Most of the twin, shown in fig.11, originates from inner ampoule wall.

3. Powder XRD Analysis:

The powder X-ray diffraction pattern (fig.12) using diffractometer (Model: JEOL JD-X, 8030) exhibits the cubic zincblende pattern of binary GaSb with prominent peaks corresponding (111), (220), (400), (311) and (331) planes These peaks are in well agreement with the standard ICDD data (GaSb – PDF card No. 65-2894; InSb – PDF card No. 89-3667). At 27 ^{0}C, the lattice parameter calculated from the 2ϕ values of the peaks has value of 6.2260 A^o. The pattern of peaks was found identical along the axis of ingot and no additional peaks corresponding to GaSb or InSb phase are present.

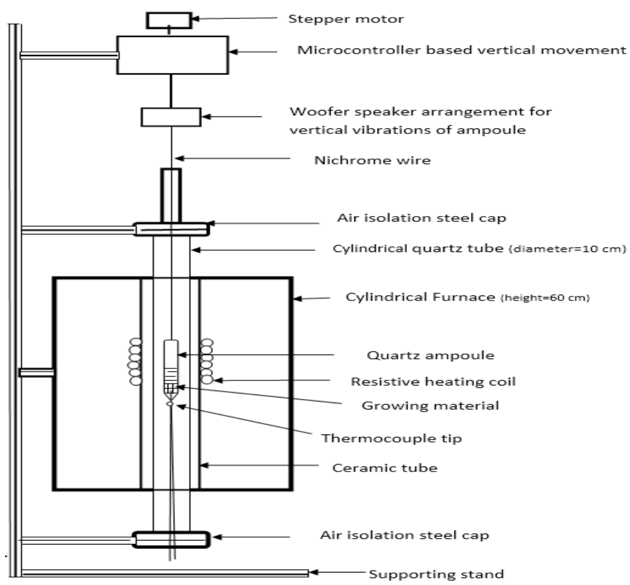

Fig.1. Schematic of VDS crystal grower

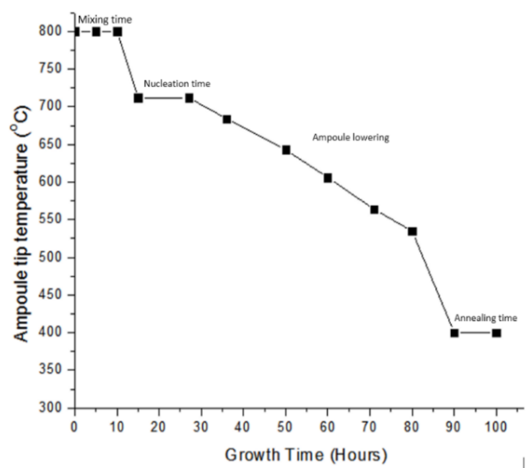

Fig.2. Growth frofile


Fig.3. cracked ampoule wall


Fig. 4. As grown ingot of $Ga_{0.9}In_{0.1}Sb$

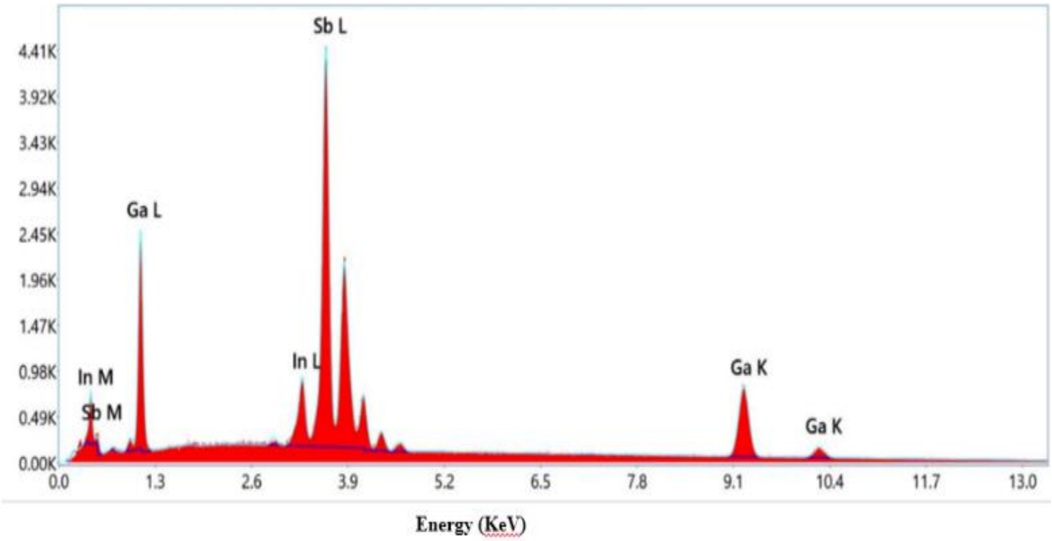

Fig.5 EDAX spectrum of $Ga_{0.9} In_{0.1}Sb$.

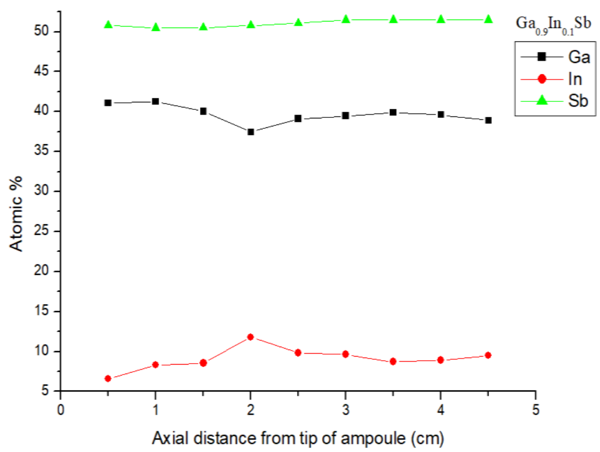

Fig.6. Compositional variation with vibration growth

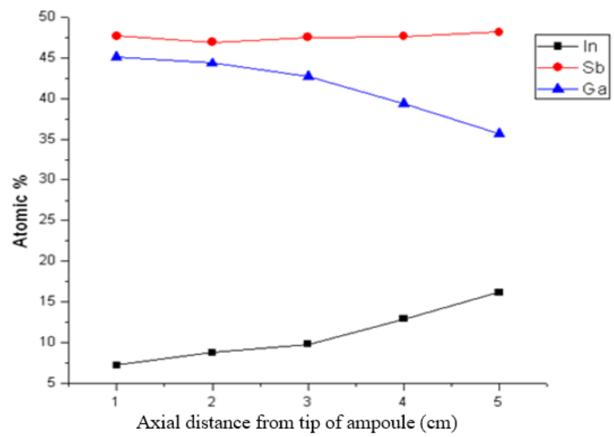

Fig.7. Compositional variation without vibration growth

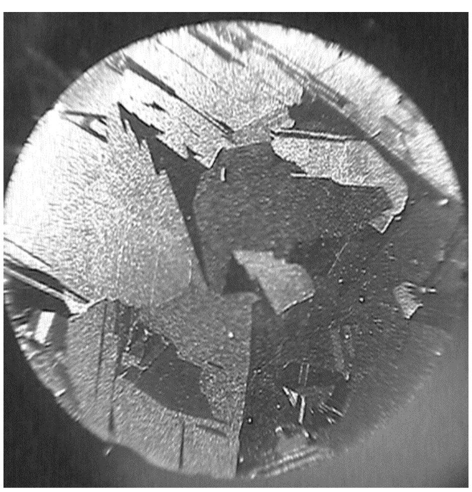

Fig.8. Grans on itched wafer (14 mm diameter)

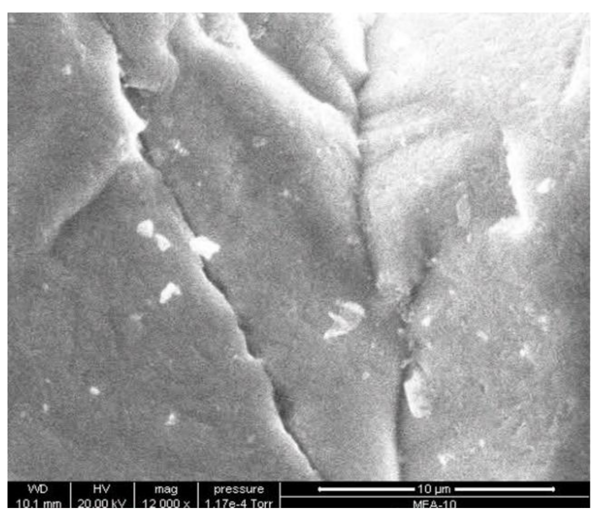

Fig.9. SEM image of microcracks

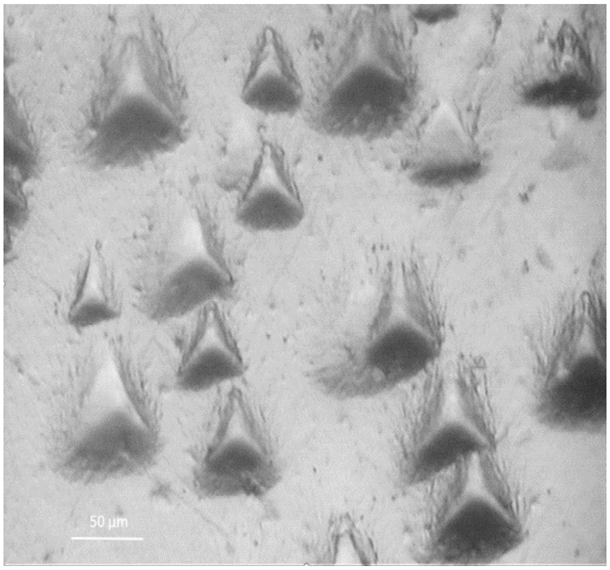

Fig.10. triangular etch pits

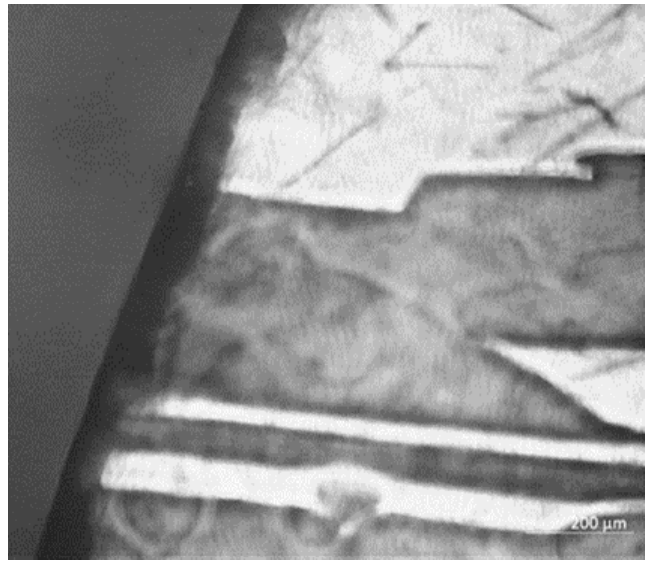

Fig.11. Twinning initiated from inner wall of ampoule

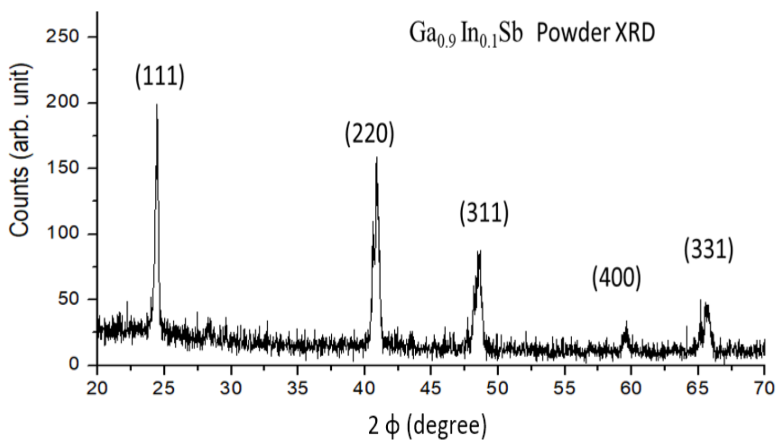

Fig.12 Powder X-ray pattern of $Ga_{0.9}In_{0.1}Sb$

Results and Discussion

Sticking of ampoule with ingot was not observed in both experiments. This indicates that unreactive indium is not present at boundary between growing crystal and inner surface of ampoule wall. This might be due to planner solid-liquid interface shape during the growth. However, cracking of ampoule was observed in both the growths. The similar ampoule cracking was reported by C marin et al [17]. In both the experiments, cracking occurs when the Indium concentration in solid reaches to 10 %. The cracking of ampoule might be due to diffusion of Indium from liquid to solid by diffusion process at solid liquid interface. This diffusion may change lattice parameter of solid at interface and creates excess pressure on inner walls of ampoule. Also, for growth rate not small enough, diffusion and convections due to thermal gradient are not enough to mix the excess Indium accumulated at interface. This may result into destabilization of interface and constitutional super cooling. The composition variation revels that vibrations enhance the mixing of excess indium in liquid and reduce the possibility of breakdown of interface. The microcracks in crystals was also observed for regions of Indium concentration more than 10 mol % , as reported by S.C. Tsur et.al[18]. The reason for initially increase of Indium concentration and reaching to 11.8 % at 2 cm from tip and decrease for remaining part of ingot is not clear.

Conclusion

Vibrations has significant effect on control of axial segregation of Indium in $Ga_{0.9}In_{0.1}Sb$ crystals growth using vertical directional solidification technique and result in spatially homogenous composition. The growth rate and vibration parameters need to be optimized for specific material composition to eliminate ampoule cracking and microcracks associated with compositional inhomogeneity in grown crystals.

Conflicts of interest: The authors stated that no conflicts of interest.

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