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GRAVITATIONAL EFFECT ON GROWTH OF In_X $Ga_{1-X}Sb$ TERNARY BULK CRYSTALS

Noriaki MURAKAMI, Koji ARAFUNE, Tadanobu KOYAMA, Yoshimi MOMOSE[1], Tetsuo OZAWA[2], Yasunori OKANO[3], Sadik DOST[4], LE. H. DAO[5], Masashi KUMAGAWA[1]and Yasuhiro HAYAKAWA[1]

[1]Research Institute of Electronics, Shizuoka University, Hamamatsu, Shizuoka, Japan
[2] Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka, Japan
[3]Shizuoka University, Faculty of Engineering, Hamamatsu, Shizuoka, Japan
[4]University of Victoria, Dept. of Mech. Eng., Victoria, BC, Canada
[5]Adv. Mat. Res. Lab., Univ. du Quebec, INRS, Verennes, Qubec, Canada
Research Institute of Electronics, Shizuoka University
3-5-1 Johoku, Hamamatsu, Shizuoka 432-8011, Japan.
Corresponding author: Y. Hayakawa
Tel/Fax: +81-53-478-1310
e-mail: royhaya@ipc.shizuoka.ac.jp

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Abstract

The effect of gravity on dissolution of GaSb in InSb melt and growth of InGaSb was experimentally investigated using GaSb(seed)/InSb/GaSb(feed) sandwich samples. Two parameters were considered: (1) the inclination angle of the sample for gravity as 0°, 53° and 90°, (2) the sample diameter (D) as 9 mm and 5mm. When θ=0°, the interface was almost flat whereas the interfaces were strongly distorted when θ= 53° and 90°. The undissolved GaSb(feed) remained for θ= 0°. However, it dissolved completely for θ= 90°, and partially for θ= 53°. As the gravitational angle was increased, the growth length of uniform composition became long. The decrease of sample diameter reduced the dissolution area of GaSb. These facts indicated that the dissolution and growth processes were strongly influenced by gravity.

Keywords: gravity, convection, solution growth, InGaSb.

1. Introduction

Growth of compositionally homogeneous ternary single crystals has a tremendous significance since such crystals can be used as substrates to grow a variety of layers without a lattice mismatch. For example, InGaSb can be controlled in the region of 6.094∼6.478Å by changing the In compositional ratio. However, it is very difficult to grow homogeneous bulk crystals because of the existence of convection on Earth. Uncontrollable convection brings about the unstable growth, and polycrystals are easy to grow. Microgravity conditions provide an almost ideal environment for homogeneous crystal growth since the buoyancy-driven convection due to gravity is almost eliminated [1, 2]. Therefore, many experiments have been performed

in space environments such as recoverable satellites and the Space Shuttle. For instance, Witt et al. grew a Te-doped InSb crystal in Skylab and achieved uniform dopant distribution [3]. Nishinaga et al. and Duffar et al. showed that the quality of GaSb crystals was improved under microgravity [4, 5]. Kinoshita et al. grew PbSnTe crystals in the SL-J/FMPT mission, and demonstrated that the etch pit density was reduced [6]. The present authors investigated the mixing of multicomponent materials in the Space Shuttle [7, 8, 9], and the effect of gravity on the dissolution and growth processes using the Chinese recoverable satellite [10, 11]. We also calculated the flow patterns as a function of gravity [12].

In the international space station (ISS) under construction, the residual gravity of 10^{-4} – 10^{-5} G range remains. The crucible is inclined against the residual gravity direction in the Japanese Experimental Module (JEM) in the ISS and the angle between the crucible axis and the gravitational direction is 53°. Therefore, preliminary experiments have been done [13]. In this manuscript, the effect of gravity on the growth interface, dissolution amount and the In compositional profiles were studied for the growth of $In_{0.03}Ga_{0.97}Sb$ crystals. The inclination angle and the sample diameter are changed as parameters.

2. Experimental Procedure

Figs 1 (a),(b) show schematic diagrams of the sample configuration and the temperature gradient in the furnace. In order to prepare the samples for the experiments, GaSb and InSb crystals were grown by Czochralski method. GaSb seed crystals were single crystalline, but InSb and GaSb feed crystals were polycrystalline. They were transformed into cylindrical shape. The lengths of GaSb and InSb were 25 mm and 4 mm, respectively. The diameters of crystals (D) were selected as 9 mm and 5 mm. The GaSb seed crystal was positioned in such a way that the {111}B face be the growth surface. The cylindrical crystals were etched in a mixture of HF:HNO_3:CH_3COOH (1:1:3 vol. ratio) to remove the oxide layer and then inserted into a BN tube followed by putting into a quartz tube as shown in *Fig. 1(a)*. Carbon sheets were used to reduce the influence of liquefaction contraction on the crystal growth process. BN tube and carbon sheets were baked to about 800°C before putting into quartz tube in Ar gas. The ampoule was evacuated to 10^{-5} Pa, and then sealed off. A thermocouple for reference was positioned just out of sample. *Figs 1(c)* and *(d)* show an outside view of an ampoule and an outside view of a sample before an experiment. The white portion is the BN tube and the blacks are carbon sheets. GaSb(seed)/InSb/GaSb(feed) crystals were stacked and the interfaces of GaSb(seed)/InSb and InSb/GaSb(feed) were clearly seen as indicated by H-I and H'-I', respectively.

The sample was set in a gold mirror furnace as shown in *Fig. 2*. The furnace was inclined 0°, 53°, 90° for gravitational direction. The seed and the feed were located at the low and high temperature regions, respectively. The temperature gradient 0.6°C/mm was used in the growth of $In_{0.03}Ga_{0.97}Sb$ crystals. The temper-

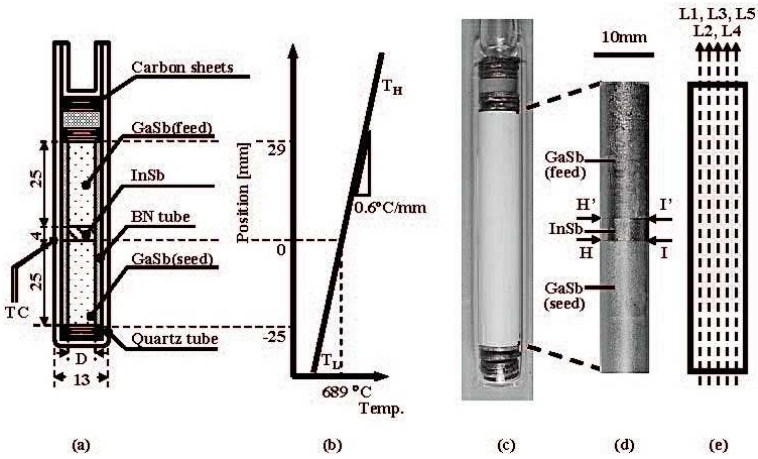

Fig. 1. (a) Sample configuration, (b) temperature distribution in the furnace, (c) an outside view of a ampoule before an experiment, (d) an outside view of a sample before an experiment, and (e) definition of the EPMA measurement lines.

ature in the furnace was changed according to the programme, but the temperature gradient was maintained during experiment. A reference temperature at the initial GaSb(seed)/InSb interface was raised up to the growth temperature T_H at a rate of 600°C/hr and then kept at that temperature for 20 hr. Later, the temperature was decreased at a rate of 6°C/hr. In growth of $In_{0.03}Ga_{0.97}Sb$ crystal, the growth temperature T_H was determined as 689°C from the InSb-GaSb binary phase diagram as shown in *Fig. 3* [14]. After the sample was heated up to 525°C (melting point of InSb), the InSb melt formed, and subsequently the GaSb crystals on both sides started to dissolve into the InSb melt and began to form an InGaSb solution. Following the dissolution formation, the InGaSb crystal was grown on the GaSb seed. The GaSb deficiency in the InGaSb solution occurred during growth due to the segregation, compensated by the dissolution of the GaSb feed.

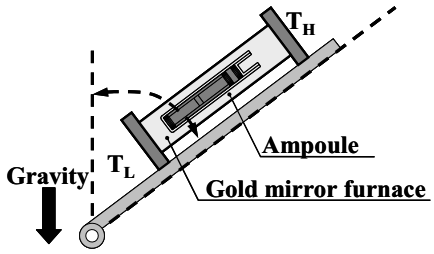

Fig. 2. Schematic diagrams of furnace arrangement.

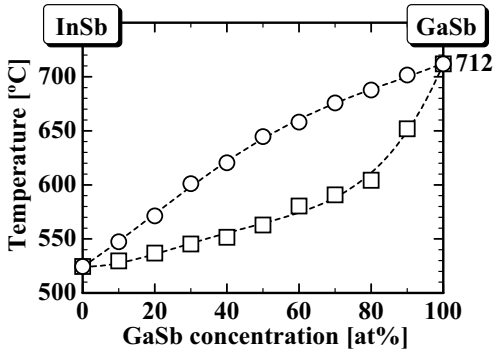

Fig. 3. InSb-GaSb binary phase diagram.

At the completion of the experiments, grown crystals were carefully removed from the quartz and BN tubes, and then an optical characterization was performed. Crystals were cut along the plane defined by the symmetry axis of the crystal and the gravitational direction. On the cut surface, the dissolution area was measured by Electron Probe Micro Analysis (EPMA). *Fig. 1(e)* indicates the definition of the EPMA measurement lines. The interval of measurement lines was 2 mm for the crystals of 9 mm in diameter, and was 1 mm for those of 5 mm in diameter.

3. Results and Discussion

3.1. Effect of Gravitational Direction

Fig. 4 shows photographs of outside views and cut surfaces of samples after experiments at different inclination angles of (a) θ=0˚(vertical), (b) θ=53°(inclined), and (c) θ=90˚(horizontal). In the case of $\theta = 90^\circ$, a big hollow was seen at the top part of the original InSb crystal. As the respective densities of solid InSb and liquid InSb were 5,780 and 6,320 kg/m^3, the volume was decreased when the InSb crystal melted. The carbon sheets were used to adjust the volume change, but the spring effect was not enough in this experiment. Hence, the liquid moved down due to gravity. When the InGaSb grew, the volume expansion should occur. However, the total volume reduced since the density of the solid InGaSb was larger than that of the solid InSb. As a result, the hollow did not disappear. On the other hand, the hollow was not formed when θ=0° and 53°. Since GaSb(feed) could move downward due to its weight in the case of $\theta = 0^\circ$ and 53°, the hollow space disappeared.

As mentioned before, GaSb(seed) dissolved into InSb melt before InGaSb crystal grew to form InGaSb solution. This means that the interface between GaSb(seed) and InGaSb grown crystal shifted to GaSb(seed) side. The interfaces can be clearly seen in the outside views as shown in *Fig. 4*. In the case of θ=0°, the

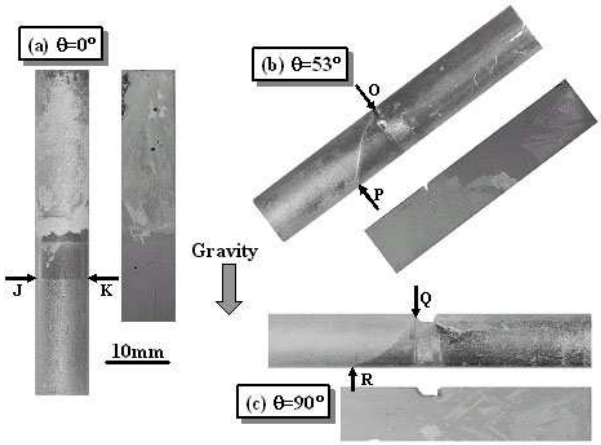

Fig. 4. Images of outside views and cut surfaces of samples after experiments at different inclination angles of (a) θ=0°, (b) θ=53°, (c) θ=90°.

interface was almost flat and parallel to the original interface of GaSb(seed)/InSb as indicated by J-K. Oppositely, when θ=53° and 90°, the interfaces were strongly distorted as indicated by O-P and Q-R. The interface curved above lower temperature region when θ=53° and under lower temperature region when θ=90°. These results indicated that the interface shape became flatter by decreasing the angle from θ=90° to $\theta = 0°$, and the shape of θ=53° was intermediate between θ=90° and θ=0°. Our experimental results clearly showed that the shape of the growth interface was strongly affected by gravitational direction.

Fig. 5 shows the dissolution area (gray colored) at different inclination angle of (a) θ=0°, (b) θ=53°, and (c) θ=90°. The undissolved GaSb feed remained for θ= 0°. However, it completely dissolved for θ= 90°, and partially remained for θ= 53°. As the thermal and solutal buoyancy convections were weak when θ= 0°, the GaSb feed was left undissolved. When θ=90°, dissolved GaSb from the solution/GaSb(feed) interface moved upward along the interface. Because this flow direction of solutal buoyancy convection was the same as that of thermal buoyancy convection, the dissolution was considerably enhanced by both convections. As a result, GaSb(feed) dissolved into the solution and disappeared as shown in *Fig. 5(c)*. When θ=53°, dissolved GaSb from the solution/GaSb(feed) interface moved upward until the interface became perpendicular to the gravitational direction. After then, the dissolved GaSb stagnated near the interface, and the dissolution was suppressed. Therefore, the dissolution area was larger than that in the case of θ=0°, but GaSb(feed) still remained.

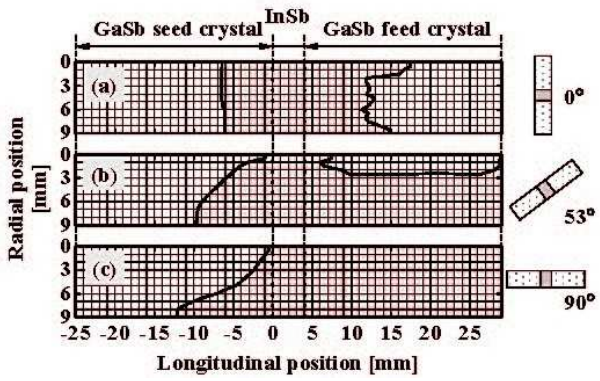

Fig. 5. Dissolution area at different inclination angles of (a) θ=0°, (b) θ=53°, and (c) θ=90° (D=9 mm).

3.2. Convection at Dissolution Process

In order to explain the difference of interface shape, the convection patterns during the dissolution process are considered as follows. *Fig. 6* shows the schematic representation of the dissolution processes. In our growth system, as temperature and concentration fields in the solution were inhomogeneous, the density of the solution was also inhomogeneous. As a result, thermal and solutal buoyancy convections existed in the solution. When θ=0°, the region at higher temperature was located above than at lower temperature. Since the density of the solution at the higher temperature was smaller than that at the lower temperature, convective instability due to temperature difference was negligible small. As the respective densities of liquid GaSb and liquid InSb are 6,010 and 6,320 kg/m^3, dissolved GaSb tended to move upward. As the interface was almost flat as shown in *Fig. 4(a)*, the flow structure in the solution might be axisymmetric as shown in *Fig. 6(a)*. When θ=90°, there were two flows due to solutal buoyancy convection. One was near GaSb(seed), and its direction was clockwise. The other was near GaSb(feed), and its direction was counterclockwise. Since the temperature at the feed side was higher than that at the seed side, the dissolved amount of GaSb at the feed side was larger than that at the seed side. The direction of thermal convection was the same as that of solutal convection near the feed side, the strength of flow at the feed side was larger than that at the seed side. As a result, the flow at the seed side was localized around the bottom region. Since the amount of Ga composition increased in the upper region of the solution, the dissolution of GaSb was suppressed. On the other hand, in the lower region of the solution, as the GaSb composition was insufficient, the dissolution of GaSb was enhanced. As a result, the dissolved area broadened towards the bottom as shown in *Fig. 4(c)*. When θ=53°, the flow pattern approached the case of θ=0°. Therefore, the interface shape of θ=53° was inter-

mediate between θ=90° and θ=0°. To make clear the flow patterns exactly, a direct flow observation is necessary.

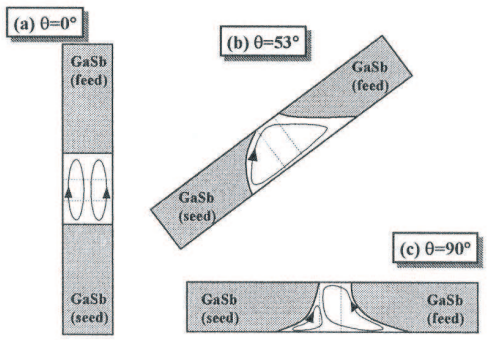

Fig. 6. Schematic representation of dissolution process. (a) θ=0°, (b) θ=53°, and (c) θ=90°.

3.3. Composition of Growth Crystal

The In compositional profiles in the InGaSb grown crystal were measured along the lines L1∼L5 as shown in *Fig. 1* and the values of L1, L3 and L5 were shown in *Fig. 7*. The qualitative analysis was done near the GaSb(seed) to investigate the absolute values in the crystal. Longitudinal position 0 mm indicates the original interface between GaSb(seed) and InSb. The gray coloured line indicates that In value was 0.03 with a fluctuation of 0.005. In the case of θ=0°, In compositional distribution at L1 was almost the same as that at L5, but was different from that at L3. The lengths of the uniform region were 6 mm at L1 and L5, but the length was 4 mm at L3. After uniform region, the In composition increased gradually along the longitudinal direction. As the segregation coefficient of In was less than unity, the rejected In was accumulated at the interface. To grow homogeneous InGaSb crystal, the lack of GaSb component has to be supplied to the growth interface by dissolving GaSb feed into solution. This result suggested that supply of GaSb was insufficient around L3. In the case of θ=53° and 90°, as the shapes of GaSb(seed)/solution interfaces were distorted, the In composition began to appear at the different positions. Moreover, the compositional uniform lengths were different in each line. Compared with the In compositional distributions at different inclination angles, it was found that the uniform length in the horizontal set up crystals (θ= 90°) are the longest of all. It may be because the dissolved region was the largest of all. This harmonized with the consideration based on the results of dissolution processes. After uniform region, In composition sometimes jumped

higher value. Since decrease of temperature caused deficiency of GaSb supply from the feed, the crystal growth stopped for a while. After the temperature at the interface reached equilibrium temperature of the solution, the growth restarted with high In composition.

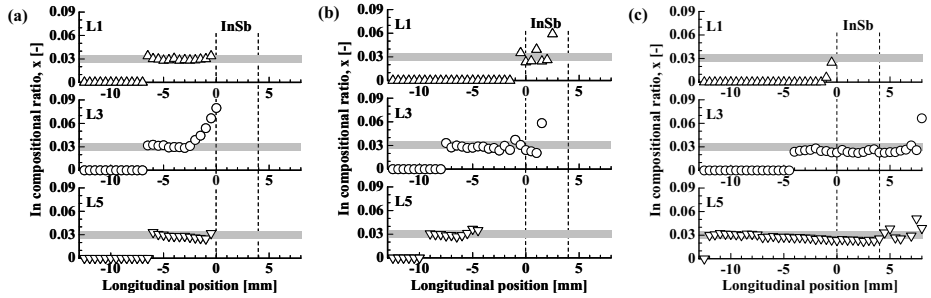

Fig. 7. In compositional profiles at different inclination angles of (a) θ=0°, (b) θ=53°, and (c) θ=90° (D=9 mm). The In compositional profiles in the InGaSb grown crystal were measured along the lines L1∼L5 shown in *Fig. 1(e)* and the values of L1, L3 and L5 were shown.

3.4. Effect of Sample Diameter

In order to investigate the effect of sample diameter on the interface shape, the sample diameters were changed as 9 mm and 5 mm. *Figs. 8(a), (b)* show the outside view, cut surface and schematic representation of the dissolution area at (a) 9 mm, (b) 5 mm. The GaSb(seed)/InGaSb interface of the two samples were broadened in the gravity direction. However, comparing with *Fig. 8(a)* and *(b)*, the dissolved length of GaSb(seed) was quite different. It was about 12 mm for the sample of D=9 mm, and about 5 mm for the sample of D=5 mm. The length of the dissolved section was smaller for the sample of smaller diameter. This clearly shows the presence of convection in the solution. Otherwise, since the length of the InSb section was fixed at 4 mm in both experiments, the length of the dissolved GaSb could have been the same in both cases if there was no convection. The reduction in the dissolved length suggests that the strength of convection was smaller in the sample of smaller diameter due to reduced convection in the solution.

4. Summary

In order to investigate the effects of gravitational direction on the dissolution of GaSb crystal into InSb melt and the growth of InGaSb, the experiments were per-

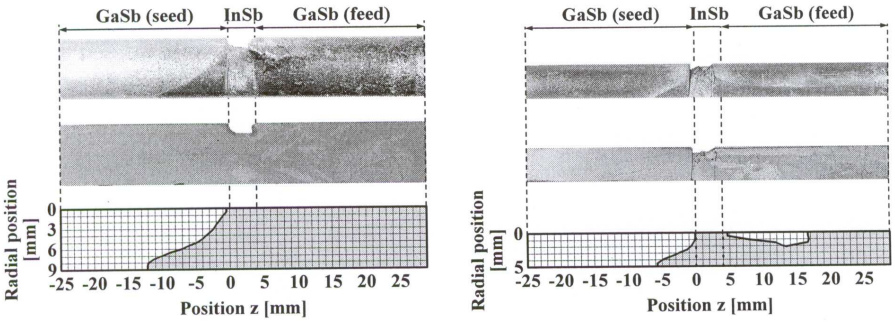

Fig. 8. Outside view, cut surface and schematic representation of the dissolution area at θ=90°. The sample diameter is (a) D=9 mm and (b) D=5 mm,

formed in the gold furnace with different inclination angles (θ for gravitational direction, such asg 0° (vertical), 53°(inclined), and 90° (horizontal).

1. When θ=90°, a big hollow was formed at the top part of the original InSb crystal, because the liquid moved down due to gravity. On the contrary, there were no hollows in the crystals of θ=0° and 53°.
2. When θ=0°, the interface was almost flat and parallel to the original interface of GaSb(seed)/InSb. On the other hand, the interfaces were strongly distorted when θ= 53° and 90°.
3. The undissolved GaSb feed remained for $\theta = 0°$. However, it completely dissolved for θ= 90°, and partially remained for $\theta = 53°$.
4. The amount of GaSb(feed) dissolution was found to decrease with the decrease of diameter.

These facts indicated that the dissolution and growth processes were strongly influenced by gravity.

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