Crystal Growth of Ternary Alloy Semiconductor and Preliminary Study for Microgravity Experiment at the International Space Station

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Crystal growth of alloy semiconductor has been under investigation at the International Space Station (ISS) to investigate growth kinetics at the solid-liquid interface, because microgravity can suppress the natural convection. In this study, we focused on InGaSb which is one of the promising ternary alloy semiconductors. As a preliminary experiment, wetting angle between the InGaSb and the materials of the ampoule and cartridge, such as quartz, carbon sheet, BN, and C-103 alloy, were measured to check their affinity of the configuration. The InGaSb exhibited much higher wetting ability on the C-103 substrate than that on the other substrates (quartz, BN, and graphite), and this result suggested C-103 can prevent leakage of the InGaSb samples in case the ampoule collapses in the cartridge. On the other hand, BN and graphite exhibited low wetting abilities with InGaSb; therefore, they are suitable materials for the ampoule because they do not significantly affect the InGaSb crystal growth. In another preliminary experiment, concentration of Te dopant, which was added to make striation in the grown crystal, was measured using inductively coupled plasma mass spectrometry (ICP-MS). It is confirmed that Te concentrations were relatively higher at the striation area.

Key Words: Alloy Semiconductor, Crystal Growth, InGaSb, Thermal Property

1. Introduction

Alloy semiconductor materials are highly useful in a variety of applications. InGaSb is one of the ternary alloy semiconductor and emitting and receiving wavelengths can be controlled in the range 1.7-6.9 μm , therefore it is used for thermophotovoltaic and infrared detector applications^{1, 2)}. However, it is very difficult to grow single crystal of high quality because of segregation-related problems and instability at the solid-liquid interfaces. It is necessary to understand the growth mechanisms to grow larger and higher quality crystals while controlling their compositions for commercial applications. To understand the growth mechanisms, experiments performed under the microgravity in space are useful, because microgravity can suppress the natural convection. Therefore, we have prepared InGaSb crystal growth experiments named "Alloy semiconductor project"³⁾ that will be performed in the Japanese module "Kibo" on the International Space Station (ISS), in order to make clear (1) the effect of the natural convection and diffusion on the alloy semiconductor crystal growth and (2) the effect of surface orientation on the growth mechanism.

To perform the experiment, it is demanded to prepare the ampoule and cartridge, which are set in the apparatus named Gradient Heater Furnace (GHF). Figures 1 (a) and (b) show a configuration of the ampoule and a cartridge used for the microgravity experiment, respectively. The ampoule consisted of a GaSb/InSb/GaSb sandwich sample and graphite sheets which were inserted into a BN tube, and sealed in a quartz

tube under high vacuum (10^{-4} Pa). The cartridge was made of C-103 alloy which exhibits chemical and thermal stability and tolerance for creep phenomena. As per the sample configuration, the sample has direct contact with BN and graphite material. Therefore, it is required to investigate the wetting properties between InGaSb and BN, graphite, and quartz. The wetting property is crucial in crystal growth because contact angles of the melt on the crucible material have important effects on the shape and quality of the crystals. In this study, in order to confirm the affinity of the configuration of the sample, the wetting angle of InGaSb on the various substrates, such as quartz, carbon sheet, BN, and C-103 alloy, that are the components of the ampoule and cartridge, was measured.

So far, we have carried out the preliminary crystal growth experiments on the ground (under 1G) with same configuration of GHF as the apparatus, and with samples in the ampoule and cartridge. Te was added as an impurity (1×10^{19} atoms/cm³) in the InSb for creating striations in the grown InGaSb by the heat pulse method during the crystal growth experiment. The composition of the grown crystal $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ became $x=0.03$ when the growth temperature was 690°C, following the phase diagram. In this study, the striation was induced in the grown crystal (Fig. 2) by the heat pulse increasing the growth temperature from 690°C to 700°C, as the Te was concentrated by the change of the growth temperature⁴⁾. From the position and the shape of the striations, crystal growth rate and the shape of the interface can be estimated. However, the concentration profile of Te in the

striation area has not been investigated so far. In this study, not only the wetting ability results, we also report the results using the inductively coupled plasma mass spectrometry (ICP-MS) measurement for quantifying Te concentration in the grown crystal.

Fig. 1. (a) The sample configuration in quartz ampoule and (b) the cartridge (made of C-103 alloy) for the experiment on the ISS.

Fig. 2. (a) Striations in the InGaSb grown crystal, (b) the heat pulse method.

2. Experimental

2.1. Wetting property

In order to confirm the affinity of the sample to the ampoule and C-103 cartridge, the wetting property of the sample was

measured on the material, which are the component of ampoule and cartridge.

The GaSb, InSb, and $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ samples ($x = 0.2, 0.4, 0.6,$ and 0.8) were prepared with the desired compositions by mixing and melting the 6N purity source materials under nitrogen atmosphere. $2 \times 2 \text{ mm}^2$ samples of each $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ composition were placed on a substrate material such as quartz, BN, graphite, and C-103. The diameter and thickness of the substrates were 10 and 5 mm, respectively. Before the experiment, the samples were cleaned with distilled water and acetone. Figures 3 (a) and (b) show the images of a sample cell before and after the experiment, respectively. The temperature of the sample was controlled using a Pt-Rh thermocouple, which was connected to the sample cell unit. The images of the wetting, the wetting angle, and the density of the melt were measured during the increase to the reference temperature ($1100 \text{ }^\circ\text{C}$). All the measurements were performed under Ar atmosphere.

Fig. 3. The sample with the substrate (a) before the experiment, and (b) after the experiment.

2.2. ICP-MS measurement of concentration of Te dopant

InGaSb crystal with striation including Te dopant was measured using ICP-MS. The crystal was cut at cross section with parallel to the growth direction, and then mirror polished with alumina powder. After mirror polishing, the surface was chemically etched with $\text{HF}:\text{KMnO}_4:\text{CH}_3\text{COOH}$ (1:3:1) for 30 min at room temperature to observe the striations. Fig. 4 shows the image of InGaSb crystal with striations observed by the differential interference contrast microscope. In the image, vertical white stripes are the striation and the interface between seed and grown crystal is suggested by a blue arrow.

The shape of the interface between seed and grown crystal is convex to the right, however, the shape of the most of

Fig. 4. Image of InGaSb crystal with striations observed by the differential interference contrast microscope.

Sample	GaSb		$\text{In}_{0.2}\text{Ga}_{0.8}\text{Sb}$		$\text{In}_{0.4}\text{Ga}_{0.6}\text{Sb}$		$\text{In}_{0.6}\text{Ga}_{0.4}\text{Sb}$		$\text{In}_{0.8}\text{Ga}_{0.2}\text{Sb}$		InSb	
Temperature (°C)	900	1100	900	1100	900	1100	900	1100	900	1100	900	1100
Quartz substrate												
BN substrate												
Graphite substrate												
C-103 substrate												

Fig. 5. Wetting images of the sample on various substrates as a function of temperature.

striations are convex to the left. It can be suggested that the melt back of center part is slower than the surroundings, and this phenomena cause GaSb rich region in melt at the surrounding part. It is indicated that striation shape, that is suggested the interface between grown crystal and melt at heat pulse, became convex to the left because the higher GaSb concentration in the melt cause the increase of growth rate at the surrounding area.

ICP-MS apparatus was consisted of laser ablation (New Wave Research Inc., UP213) and the apparatus of ICP (Agilent Technology Inc. 7500x). In this study, we scanned cross section of the crystal from seed to grown crystal through the striation region (Fig. 4). The diameter of laser beam was 20 μm and the scan rate was 2 $\mu\text{m}/\text{sec}$.

3. Results and Discussion

3.1. Wetting property

The contact angle between the melt and the substrate surface indicates the degree of wetting. A surface is completely wetted if the contact angle formed by the melt on the substrate surface is 0° and is completely non-wetted if the contact angle is 180°. The contact angle depends on the solid-melt surface energy. From the images of the wetting, the wetting angle and the density of the melt were measured.

Fig. 6. Wetting angle of InGaSb melt on (a) the quartz, (b) BN (c) graphite, and (d) C-103 substrates as a function of temperature.

Figure 5 shows the images of the wetting of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ samples on the quartz, BN, graphite, and C-103 substrates at 900 and 1100 °C. It demonstrated clearly that the wetting of the C-103 was superior compared with other substrates. Figures 6 (a)-(d) show the wetting angles of GaSb, InSb, and $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ on the quartz, BN, graphite, and C-103 substrates, respectively. The wetting angles are plotted as functions of temperature. These results indicated that BN and graphite had low wetting ability, and quartz had slightly higher wetting ability than that of BN and graphite. C-103 had the highest wetting ability among the other substrates. The wetting angle of GaSb was larger than that of InSb on the quartz and BN substrates at high temperature. The result suggests that the degree of the reaction between InSb and the substrates was higher than that of GaSb and the substrates. The wetting angles of $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ ($x = 0.2, 0.4, 0.6$, and 0.8) were between those of GaSb and InSb.

As shown in Figs. 5 and 6 (d), the wetting of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ samples on the C-103 substrate was much higher than the quartz, BN, and graphite substrates. This difference was significant and the result suggests that the interaction between $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ and the C-103 substrate was strong. The samples adhered strongly to the C-103 substrate after they were solidified, which also suggests that the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ melt exhibited a strong interaction with C-103 substrate.

Moreover, it is obvious that the wetting angles decreased with increasing the temperature. These results indicate that both BN and graphite materials, which have no wetting ability with the samples, are suitable as materials for the ampoule because they have direct contact with the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ sample during the crystal growth experiment. In addition, the high wetting ability of C-103 means that C-103 can prevent the leakage of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ samples in case the ampoule collapses inside the cartridge, because the InGaSb sample will spread over the interior of the cartridge. Therefore, a C-103 cartridge is suitable for the microgravity experiments.

Fig. 7. Density of InSb, InGaSb ($x=0.2, 0.4, 0.6$ and 0.8) and GaSb samples at 900 °C on the BN substrates.

Figure 7 shows the density of the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$, InSb and GaSb corresponding to its composition. The density was calculated using the volume estimated from the images of the melted samples on the substrates and the masses of the samples. It is indicated that the density of $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ increased with increasing In composition.

3.2. ICP-MS measurement of concentration of Te dopant

Figure 8 shows the Te ion intensity profiles along scan distance measured by ICP-MS. The results were compared with the differential interference contrast microscope image. In the figure, Te ion intensity was increased at the interface between the seed material and grown crystal. When comparing the differential interference contrast microscope image with ICP-MS data, it is obvious that the Te ion intensity increased at the striation area. It is suggested that Te dopant concentrated at the striation area due to heat pulse, because when we introduce heat pulse, crystal growth temperature increased and grown crystal melt back. After the holding period, temperature decreased rapidly to initial value and thus crystal was rapidly grown with high growth rate during cooling cycle of heat pulse. The Te concentration in the rapidly grown region was larger compared with the other area due to change in effective segregation coefficient with growth rate⁴⁾. The results of ICP-MS supported the formation mechanism of striations.

Fig. 8. Te ion intensity profiles detected using ICP-MS and the differential interference contrast microscope image. Dashed line shows the position of striation in InGaSb grown crystal.

4. Conclusion

The wetting property of InSb, GaSb, and $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ on the quartz, BN, graphite and C-103 substrates was analyzed at two different temperatures. The InGaSb exhibited much higher wetting ability on the C-103 substrate than that on the other substrates (quartz, BN, and graphite). BN and graphite exhibited low wetting abilities with $\text{In}_x\text{Ga}_{1-x}\text{Sb}$, so they are suitable materials for the ampoule because they do not significantly affect the $\text{In}_x\text{Ga}_{1-x}\text{Sb}$. In addition, concentration of Te dopant, which was added to make striations in grown crystal, was measured using ICP-MS. It was confirmed that Te

concentration was relatively higher at the striation area.

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References

- 1) Bachmann, K. J., Thiel F. A. and Schreiber Jr. H.: Melt and Solution Growth of Bulk Single Crystals of Quaternary III–V Alloys, *Prog. Crystal Growth Characterization*, **2**, (1981) pp.171-206
- 2) Dutta, P. S., Bhat, H. L. and Kumar, V.: The Physics and Technology of Gallium Antimonide: An Emerging Optoelectronic Material, *J. Appl. Phys.* **81**, (1997) pp. 5821- 5871.
- 3) Arivanandhan, M., Rajesh, G., Tanaka, A., Ozawa, T., Okano, Y., Inatomi, Y. and Hayakawa, Y.: Bulk Growth of InGaSb Alloy Semiconductor Under Terrestrial Conditions: A Preliminary Study for Microgravity Experiments at ISS, *Diffusion and Defect Forum*, **323-325**, (2012) pp. 539-544.
- 4) Murakami, N., Hikida, T., Konno, A., Arafune, K., Koyama, T., Momose, Y., Ozawa, T., Miyazawa, M., Kumagawa, M. and Hayakawa, Y.: Growth of Homogeneous InGaSb Ternary Alloy Semiconductors on InSb Seed, *J. Crystal Growth*, **310**, (2008), pp. 1433-1437 .