J. Jpn. Soc. Microgravity Appl. Vol. 28 No. 2 2011 (S46–S50)

8th Japan-China-Korea Workshop on Microgravity Sciences
for Asian Microgravity Pre-Symposium

Crystal Growth of InGaSb Alloy Semiconductor at International Space Station: Preliminary Experiments

Mukannan ARIVANANDHAN [1], Govindasamy RAJESH [1], Tadanobu KOYAMA [1], Yoshimi MOMOSE[1], Krishnasamy SANKARANARAYANAN[1], Akira TANAKA [1], Yasuhiro HAYAKAWA[1*], Tetsuo OZAWA[2], Yasunori OKANO[3] and Yuko INATOMI[4]

Abstract

As a preliminary experiment for the near future microgravity experiment, $In_xGa_{1-x}Sb$ bulk crystal was grown under 1G condition using GaSb(seed)/InSb/GaSb(feed) sandwich sample. In order to prepare the seed and feed crystals for GaSb(seed)/InSb/GaSb(feed) sandwich sample, GaSb single crystals with different orientations viz., <100>, <110>, <111> were grown by CZ method. Moreover, heavily (1×10^{20} cm^{-3} in solution) tellurium (Te)-doped poly crystalline InSb sample was synthesized to prepare the sandwich sample. The effect of various heat pulses on the Te-impurity induced growth striations was investigated by introducing various kinds of heat pulses during the growth experiment. An appropriate heat pulse which is capable to produce a clear and thin striation was identified. Based on the observed growth striations, the growth rate of the crystal was roughly estimated.

1. Introduction

More than three decades, the role of gravity on the understanding of growth mechanism of various materials including the narrow band gap semiconductors such as Ge (0.66 eV), GaSb (0.72 eV), InSb (0.17 eV) were investigated [1)-4)]. In general, the microgravity experiments focus on the growth of perfect crystals (with low defect density) due to dominated diffusive transport in space. In this aspect, Nishinaga et al[2)], reported that the high-quality tellurium (Te) doped GaSb crystal was grown by gradient freezing method in a Chinese recoverable satellite. Moreover, it was also demonstrated that the etch-pit density tends to zero in the space grown GaSb sample, where the melt did not touch the ampoule wall, but it increased steeply in the part where strong contact with the wall occurred. Just one year later, Duffar et al, have reported that the quality of GaSb and InGaSb crystals were improved when they were grown without contacting crucible under microgravity[3)].

In this series, we have carried out several microgravity experiments using a space shuttle, a drop tower, and a Chinese recoverable satellite[5)-8)]. The effect of diffusive transport and surface tension induced convection (Marangoni convection) on the mixing of multi-component melts was investigated in the space shuttle using In/GaSb/Sb sandwich sample[6)]. The role of gravity on the shape of solid – liquid interface and composition profiles were clarified by comparing the experimental results on the Chinese recoverable satellite and on earth[7),8)]. Moreover, the effect of gravitational direction on the dissolution and growth of InGaSb were investigated by inclining the furnace with different inclination angles on earth[9)]. Recently, the dissolution process and solute transport in the GaSb (seed)/InSb/GaSb (feed) sandwich sample were in-situ observed by X-ray penetration method[10)]. The result shows that the gravity induced solutal transport was strongly influenced in the dissolution process and the numerical results obviously support the experimental observations[11)].

In the present report, we have made some preliminary experiments in connection with our near future microgravity experiments to grow high quality InGaSb alloy crystals using Gradient Heating Furnace (GHF) at International Space Station (ISS) and the results are reported. To prepare seed and feed crystals for GaSb(seed)/InSb/GaSb(feed) sandwich sample, GaSb single crystals with different orientations viz., <100>, <110>, <111> were grown by CZ method. InGaSb bulk crystal was grown under 1G condition using cylindrical shaped GaSb <111> seed crystal. The purpose of the present experiment is to find a suitable heat pulse which can able to produce a clear striation in the grown crystal. For this purpose, various kinds of heat pulses were introduced during the growth. From the post growth studies, a suitable pulse which can create a clear striation was identified and it will be used in our future microgravity as well as terrestrial experiments to create striation in the grown crystal.

1 Research Institute of Electronics, Shizuoka University, Johoku 3-5-1, Naka-ku, Hamamatsu 432-8011, Japan
2 Department of Electrical Engineering, Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka 437-8555, Japan
3 Graduate school of Engineering Science, Osaka University, 1-3 Machiganeyama, Osaka 560-8531, Japan
4 Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Kanagawa 229-8510, Japan
(*E-mail: royhaya@ipc.shizuoka.ac.jp)

2. Experimental Procedure

Figure 1 shows schematic diagrams of (a) the sample configuration, (b) the temperature distribution in the furnace, an outside view of a sample filled ampoule before the experiment (c) and the photograph of the sample (d). The growth experiment was performed using a sandwich sample in which, InSb was placed between GaSb single-crystal (seed) and poly crystal (feed). In **Fig. 1**(d), GaSb (seed)/InSb/GaSb (feed) crystals were stacked and the interfaces of GaSb (seed)/ InSb and InSb/GaSb(feed) were clearly seen. In Fig. 1(c), the white portion is the BN tube and the blacks are carbon sheets. In order to prepare the seeds for preliminary experiments as well as space experiments, number of GaSb single crystals were grown along three different orientations such as <111>, <110> and <100> by the Czochralski (CZ) method. The pulling and rotation rates of the crystals were 2-4 mm/h and from 1 to 10 rpm, respectively. The growth conditions were optimized for each orientation growth. Polarities of the GaSb <111> single crystals were identified by etch pattern analyses.

For the preliminary experiments, InSb and GaSb feed crystals were polycrystalline. The CZ grown GaSb single crystals were shaped into cylindrical rod using a lathe blade. The lengths of GaSb (seed and feed) and InSb were 23 and 4 mm, respectively. The diameter of the shaped crystals is 9 mm. Subsequently, the crystals were polished by alumina abrasive to get mirror surface and then etched in a mixture of HF: HNO_3: CH_3COOH (1:1:1) to remove the oxide layers. The crystals were inserted into a BN tube and put into a quartz ampoule. For the present preliminary experiment, the <111> GaSb seed crystal was chosen and the seed was positioned in such a way that the growth plane became <111> B. The ampoule was evacuated to 10^{-4} Pa, and then sealed.

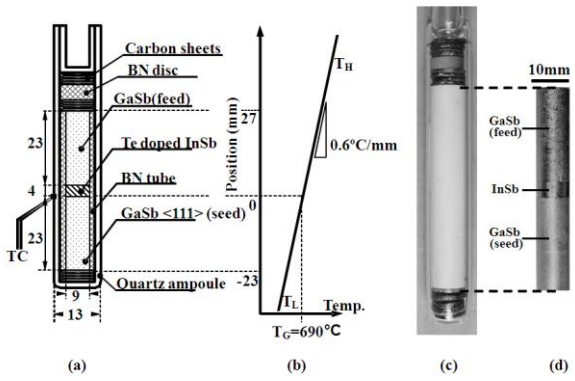

Fig. 1 (a) Schematic diagram of sample configuration, (b) Temperature profile, (c) outside view of the ampoule and (d) sample.

The furnace was heated to the pre-determined temperature profile at a proper heating rate (80 °C/h) after placing the growth ampoule in an appropriate position. The temperature gradient in the furnace was fixed as 0.6 °C/mm. Based on the reference temperature (measured by the thermocouple) and the temperature gradient, the temperature at the GaSb seed interface was determined and controlled. At the fixed temperature gradient, the furnace was heated up to the reference temperature 600 °C at a heating rate of 80 °C/h and kept at that temperature for 19 h. Once the Te doped InSb was completely melted, GaSb seed and feed were started to dissolve into the InSb melt. The dissolved GaSb at the feed interface were transported into the seed interface by solutal convection and diffusion originated from the concentration gradient due to temperature gradient. As a consequence, the solution near the seed interface gets supersaturated and thus growth was initiated from the un-dissolved GaSb seed crystal.

As shown in **Table 1** various kinds of heat pulses were applied during the growth process to investigate the effect of pulse's shape on the growth striations. In our previous investigations, we applied the heat pulses during the InGaSb growth by moving the ampoule to a high temperature-region – hold for 1 min at high temperature – and it was moved down to the original position[12]. During this kind of process the introduced heat pulse may not have sharp profile. Moreover during the ampoule movement, the growth interface may be disturbed. So, in the present investigation, instead of moving the ampoule, we increased the temperature of the furnace by keeping the ampoule at fixed position. To study the effectiveness of this process and find a suitable pulse for the future microgravity experiments, various kinds of heat pulses were applied and studied its effects on striations. For the square pulse, the furnace temperature was increased to 10 °C from the growth temperature with increasing time of 1 min and hold for various times such as 1 min, 2 min. and 4 min. Then the temperature was cooled down to initial temperature in 10 s. Although the furnace temperature was decreased to initial temperature in 10 s, the actual temperature of the sample takes more time to come to initial temperature. By considering this fact, we introduce some square pulses with positive and negative cycles. **Figure 2** shows the temperature program used for the InGaSb growth and the applied pulses were marked as P1 ,P2 … P9 with respect to growth period. Since the purpose of the present experiment is to make clear the effect of pulse shapes on the striations, the growth was conducted only for 19 h. Once the selected pulses were applied, the growth system was gradually cooled from growth temperature to 500 °C at a pre-determined cooling rate to reduce the thermal stress and cracks in the grown crystals. From 500 °C the ampoule was cooled down to room temperature as shown in **Fig. 2**. In the present experiment, 9 pulses (P1-P9) were applied at the interval of 2 h

Table 1 Different shape of heat pulses applied during InGaSb growth. The increasing time is 1 min. for all the pulses. The cooling time is 10 sec for all the positive square wave pulses and 20 sec for the positive and negative square wave pulses.

Pulses	Holding time	Shape of the pulse
P1	2 min.	Positive Square pulse
P2	2 min.	Positive Square pulse
P3	4 min.	Positive Square pulse
P4	1 min.	Positive Square pulse
P5	2 min.	Positive Square pulse
P6	2 min at both high and low temp	Positive and negative square pulse
P7	2 min at high and 1 min at low temp.	Positive and negative square pulse
P8	1 min. at both high and low temp	Positive and negative square pulse
P9	1 min at high and 2 min at low temp	Positive and negative square pulse

growth. The time interval between the pulses 4 and 5 was fixed ass 1 h to check the growth distance variation by observing the striations. The tellurium impurity concentration was modulated by the heat pulses thereby the striations were introduced in the grown crystals.

The grown crystal was cut along the growth direction and the surfaces were polished by alumina abrasives. The sample was etched in a solution of HF: $KMnO_4$: CH_3COOH (1:3:1) to observe the tellurium (Te) impurity induced striations.

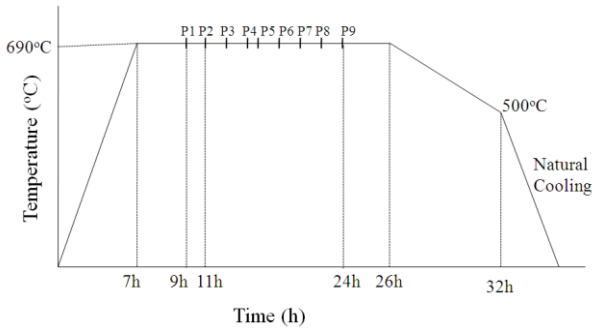

Fig. 2 Temperature program used for the growth experiment.

The indium composition profile of the grown crystal was measured along the growth direction by electron probe micro analyzer (EPMA).

3. Results and discussion

Figure 3 shows the optical microscopic image of the etched surfaces of the grown InGaSb crystal. As the purpose of the present experiment is to study the effect of pulse shapes on the striations, the growth experiment was conducted only for 19 h. As a result, about 2 mm length of InGaSb crystal with 9 mm diameter was grown. The striations which are formed by the introduction of thermal pulses were clearly seen in the etched surface of the grown InGaSb crystal. Almost all the striations produced by the square shape pulses (P1 to P5) were very sharp and clear although the holding time and increasing times were varied. Moreover, the growth distance between the pulses P4 and P5 is almost half of the distance between the pulse P5 and P6. This is possibly due to the intentionally varied time interval (1 h) between pulses P4 and P5 as shown in **Fig. 2**. On the other hand, the striations produced by the square pulses with positive and negative heating cycles (P6 to P9) were wider and thus not sharp. Moreover, the width of the striations created by the square pulses with positive and negative heating cycles was varied based on the holding time at the negative cycle in low temperature. The pulses 6 and 9 have 2 min. holding time at the low temperature whereas the pulses 7 and 8 have 1 min. holding time at low temperature (pl. refer **Table 1**). As a result, the striations created by pulses 6 and 9 are more wide compared to the striations created by pulses 7 and 8.

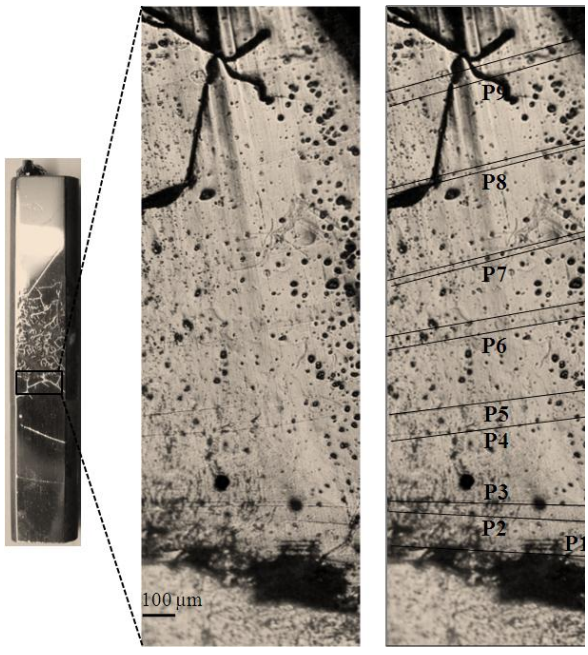

Fig. 3 Photograph of the cross section of grown InGaSb crystal and etched surface of the grown region with striations.

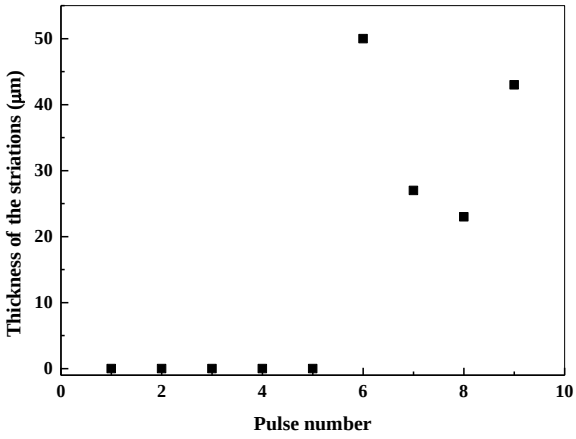

Fig. 4 Thickness variation of striations with applied pulse numbers.

Figure 4 shows the thickness variation of striations with respect to pulses numbers. Te impurity was incorporated into the In-Ga-Sb solution from the molten Te-doped InSb with the initial Te concentration of 1×10^{20} atoms/cm^3 in the In-Ga-Sb solution. The growth temperature of $In_xGa_{1-x}Sb$ crystal was fixed as 690 °C and thus based on the InSb-GaSb phase diagram, the expected composition of the crystal is $In_{0.03}Ga_{0.97}Sb$. The effective segregation coefficient of Te in GaSb crystal growth was estimated to be 0.37[13]. Therefore, for our Ga rich InGaSb crystal growth, we considered the effective segregation coefficient of Te as 0.4.

According to Tiller's theoretical investigation[14], the dopant concentration in the solid at a distance x from the seed interface of the specimen can be expressed as shown in eq 1.

$$C_s = C_0 \left\{(1-k)\left[1-\exp\left(-k\frac{R}{D}x\right)\right]+k\right\} \quad (1)$$

where, k is the segregation coefficient of impurity, $C_s(x)$ is the impurity concentration in the solid at a distance x measured from the beginning of the crystal, C_o is the initial concentration of impurity in the solution, D is the diffusion coefficient of the solute in the melt and R is the growth rate. From the eq. (1), it is obvious that two factors mainly influence the impurity distribution in liquid and the first one is the diffusion coefficient of impurity which tends to diffuse the impurity homogeneously throughout the solution and the second one is the growth rate which act as a source of impurity near the growth interface as the impurity rejected from the interface. The value of D is constant for each material[14], on the other hand R can be varied. So, from the above expression, it is clear that increasing or decreasing the rate of growth changes the impurity concentrations in the solid. Moreover the rate of change of growth rate is based on the thermal conductivity of the crystal and the latent heat of fusion.

When the heat pulse applied, the temperature at the growth interface increased and thus the grown crystal was partially melted and the Te concentration in the liquid adjacent to the growth interface was increased. Then the temperature was rapidly cooled down to initial growth temperature. During this cooling, the crystal was grown with high growth rate. Due to this high growth rate, the Te concentration in the grown crystal increased. So, Te concentration in the region grown by applying thermal pulse was higher than the region grown without a thermal pulse. By etching the crystal, the band like structures were formed since the etching rate depends on the Te concentration.

The **Figure 4** clearly shows that the striation width is based on the rate of change of growth rate thereby change of Te concentration in the crystal. The square wave shape pulses were created very sharp striations that mean the crystal was grown with higher rate during the short period of cooling. During this cooling the effective segregation coefficient of Te increased abruptly which resulted narrow region of high Te concentration in the grown crystal. On the other hand, for the square pulse with positive and negative heating cycles, despite of the same heating part, cooling part of the pulse was quite long. So that the crystal was grown for relatively long distance with higher growth rate and therefore the Te concentration was higher for quite long distance due to large effective segregation coefficient. Thus the striations created by square pulses with positive and negative cycles were relatively wider compared to striations created by square pulses.

Figure 5 schematically shows how the Te concentration varied in the grown crystal (thereby wideness of striations) during cooling cycle of the (a) positive square pulse and (b) square pulse with positive and negative cycles. The initial growth interface and the interface after rapid growth were indicated as I' and I" in **Fig. 5** (a) and (b). Moreover, the thermal conductivity of the GaSb solid (8.1 W/mK) and InSb liquid (17.7 W/mK) are larger than that of the quartz ampoule (1.62 W/mK)[15]. From the heat pulse experiment, it is obvious that the

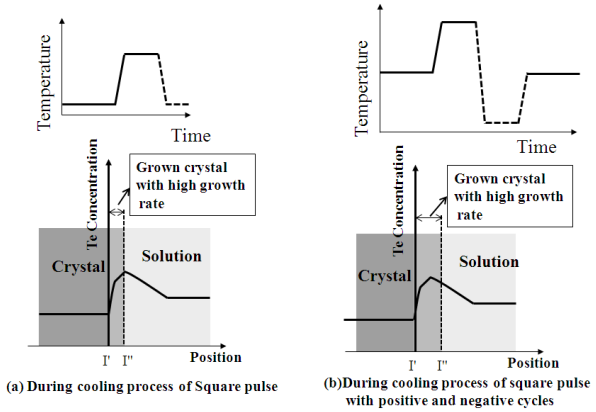

Fig. 5 Schematic representation of Te impurity concentration variation after introduction of (a) square and (b) square pulse with positive and negative cycles.

short period of cooling time (positive square pulse) is quite enough for the sample to get cooled to original temperature. Subsequently, it was inferred that the square shape pulses with only positive cycle are more appropriate for creating a sharp striations in the grown crystal rather than the square pulses having the both positive and negative cycles.

The growth rate of the crystal was calculated from the observed striations. It was found that at initial stage the growth rate was increased from 0.06 mm/h. After 10 h of growth period the growth rate reached to the value of 0.1 mm/h. From the measured growth rate, the Te concentration in the grown crystal was estimated using eq. (1). It was found that the Te concentration increased along the growth direction. The Te concentration of 4×10^{19} atoms/cm^3 was obtained at the growth distance (x) of 1.7 mm using the estimated growth rate, which is nearly one order low compared to the Te concentration in the In-Ga-Sb solution. The diffusion coefficient of 3×10^{-5} cm^2/s was used for the calculation of Te concentration in the Ga rich InGaSb solid[13]. Moreover, the indium composition of the grown crystal was measured by EPMA measurements. The indium composition measured at the GaSb seed interface was 0.05 and it was decreased along the growth direction. The equilibrium temperature correspond to the indium composition measured at the GaSb seed interface was found to be same as the temperature fixed near the growth interface position during the growth. It ascertains the optimum temperature distribution in the growth furnace.

4. Conclusion

GaSb single crystals were grown along different orientations viz., <100>, <110>, <111> by CZ method. The preliminary experiments for the microgravity experiment have been carried out to grow high quality InGaSb alloy crystals by GHF using a GaSb <111>B (seed)/Te-doped InSb/GaSb (feed) sandwich structure. The effect of various heat pulses on the Te-impurity induced growth striations was investigated. From the observed striations, it was inferred that the square shape pulses with only positive cycle are more appropriate for creating a sharp striations in the grown crystal rather than the square pulses having the both positive and negative cycles. The maximum growth rate of 0.1 mm/h was achieved after 10 h of growth period.

Acknowledgement

We thank Drs.T.Ishikawa, M.Takayanagi, K.Sakata (JAXA), T.Shimaoka (JSF), T.Sone, J.Yoshikawa (JAMSS), H.Tomioka and K.Taguchi (AES) for their support in the growth experiments. This work was financially supported by Grant-in-Aid for Scientific Research (B) (no. 22360316 and no. 23360343), and a Grant-in-Aid for Young scientist B (no. 22760005) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Part of the work was supported by the cooperative research project of the Research Institute of Electronics, Shizuoka University, Japan.

References

1) K.W. Benz, Prog. Cryst. Growt. And Charact. **26** (1993) 267.
2) T. Nishinaga, P. Ge, C. Huo, J. He and T. Nakamura: J. Crystal Growth, **174** (1997) 96.
3) T. Duffar, M.D. Serrano, C.D.Moore, J. Camassel, S. Contreras, P. Dusserre, A. Rivoallant and B.K. Tanner: J. Crystal Growth **192** (1998) 63.
4) J. Nakata, N. Kuratani, H. Tomozawa, Y. Nishimura, N. Yokogawa and I. Inagawa: Jpn. J. Appl. Phys. **37** (1998) L1396.
5) Y. Hayakawa, Y. Furukawa (Eds.), "Studies on Crystal Growth under Microgravity" Research Signpost, 2005, pp. 1-50.
6) K. Okitsu, Y. Hayakawa, A. Hirata, S. Fujiwara, Y. Okano, N. Imaishi, S. Yoda, T. Oida, T. Yamaguichi and M. Kumagawa: Jpn. J. Appl. Phys. **36** (1997) 3613.
7) T. Kimura, Y. Hayakawa, T. Ozawa, Y. Okano, A. Hirata, M. Miyazawa, N. Imaishi, K. Arafune, T. Yamaguichi and M. Kumagawa: J. Jpn. Soc. Microgravity Appl. **15** (1999) 472.
8) Y. Hayakawa, Y. Okano, A. Hirata, N. Imaishi, Y. Kumagiri, X. Zhong, X. Xie, B. Yuan, F. Wu, H. Liu, T. Yamaguichi and M. Kumagawa: J. Cryst. Growth **213** (2000)40.
9) N. Murakami, K. Arafune, T. Koyama, M. Kumagawa and Y. Hayakawa: J. Cryst. Growth **263** (2004) 320.
10) G. Rajesh, M. Arivanandhan, H. Morii, T. Aoki, T. Koyama, Y. Momose, A. Tanaka, Y. Inatomi and Y. Hayakawa: J. Cryst. Growth, **312** (2010) 2677.
11) G. Rajesh, M. Arivanandhan, H. Morii, Suzuki, T. Aoki, T. Koyama, Y. Momose, A. Tanaka, Y. Inatomi and Y. Hayakawa: Proc. of Japan society of Applied Physics, Sep. 2010.
12) N. Murakami, K. Arafune, T. Koyama, M. Kumagawa and Y. Hayakawa: J. Cryst. Growth **275** (2005) 433.
13) G. Muller, Convection and Inhomogeneities in Crystal Growth from the melt, Vol. 12, Springer, Berlin, 1988.
14) W. A Tiller, K. A. Jackson, J.W. Rutter and B. Chalmers: Acta Met. **1** (1953) 428.
15) S. Nakamura and T. Hibiya: Int. Thermophys. **13** (1992) 1061.

(Received 10 Oct. 2010; Accepted 19 Jul. 2011)