Homogeneous $In_{0.3}Ga_{0.7}As$ Crystal Growth by the Graded Solute Concentration Method

Kyoichi Kinoshita †, ††, **Hirokazu Kato** ††, **Satoshi Matsumoto** ††, **Masayuki Iwai** †††, **Tetsuya Tsuru** †††, **Yuuji Muramatsu** ††† and **Shin-ichi Yoda** ††

† NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi-shi 243-0198, Japan
†† National Space Development Agency of Japan, 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan,
††† Advanced Engineering Services Co. Ltd., 1-6-1 Takezono, Tsukuba, Ibaraki 305-0032, Japan

We have developed a new crystal growth method "the graded solute concentration method" for obtaining homogeneous mixed crystals from their melt in microgravity and further developed this method by adopting the idea of partial melting method and named as "the concentration gradient partial melting method". In the Space Shuttle or in the International Space Station, residual acceleration on the order of 10^{-3} – 10^{-4} G still remains and it causes inhomogeneous distribution of the solute, but this method compensates solute loss at the growing interface due to the residual acceleration and produces homogeneous crystals. On the ground-based experiments, single crystals of $In_xGa_{1-x}As$ with x = 0.20 – 0.33 having longer than 20 mm homogeneous parts were obtained by this method.

1. Introduction

We are planning to grow homogeneous $In_{0.3}Ga_{0.7}As$ crystals in microgravity, because $In_{0.3}Ga_{0.7}As$ is a promising material as substrates of laser diodes for the optical fiber communication system, but the growth of homogeneous $In_{0.3}Ga_{0.7}As$ single crystals is very difficult on the ground. Microgravity environments are beneficial in suppressing convection in a melt and growth of homogeneous crystals is expected. Since the successful experiments on InSb by H. U. Walter[1] and A. F. Witt *et al*[2] in the Skylab project, many investigators attempted to grow homogeneous and low defect density compound semiconductor crystals in space. However, very few satisfactory results have been obtained since then. This may be because insufficient consideration has been given to the residual acceleration and g-jitter in a melt, and purely diffusion limited growth might not be realized in the past space experiments. One of the authors designed $Pb_{1-x}Sn_xTe$ crystal growth experiment in the space shuttle mission and the compositional profile suggested partial mixing of the melt during crystal growth[3]. According to a computer simulation, the residual accelerations on the order of 10^{-6} G or less are required for the diffusion limited growth from a melt[3, 4]. To fulfill above conditions is very difficult because the residual acceleration combined with g-jitter in the space station may give effects to the melt on the order of 10^{-4} G. Therefore, new growth methods are to be invented to grow homogeneous crystals from a melt in the space station. For this purpose, we have developed the graded solute concentration method[5]. The method is further developed into a concentration gradient partial melting method and single crystals of $In_xGa_{1-x}As$ with x = 0.20 – 0.33 having longer than 20 mm homogeneous parts were obtained by this method. Here, we report on the preliminary results performed on the ground.

2. Experimental

The principle of the graded solute concentration method is shown in Fig. 1. In this method, a feed with graded solute concentration is used instead of a uniform feed. If the residual acceleration on the order of 10^{-4} G exists, it will cause weak convection and the solute at the solid-liquid (S/L) interface will be transported away from the interface by the convection. Such transportation of the solute results in the concentration profile of the solute similar to that of partial mixing of the melt during crystal growth (Fig. 1a), when a uniform feed is used. On the other hand, if the solute concentration in the feed. decreases from the top to the end as is shown in Fig. 1b, the excess solute will be compensated by the solute loss due to weak convection in the melt and will result in a uniform crystal. In this method, choosing an appropriate soaking period is important because the preinstalled concentration profile in the feed will smear out by diffusion in the melt. Solidification rate should also be determined so as to maintain constant solute concentration at the S/L interface. If weak convection exists, apparent diffusion coefficient of the solute increases. Therefore, the growth rate should be higher than the case of diffusion limited growth. In order to determine appropriate growth rate, InAs-GaAs interdiffusion coefficients were measured by the sounding rocket TR-IA#7 launched in September in 1998[6]. The result is shown in Fig. 2. The coefficients range form 1.2 to 4.1 x 10^{-8} m^2/s. According to the numerical analysis, growth rates of higher than 3 mm/h are deduced so as to obtain uniform concentration of the solute[7]. However, these growth rates are too high in the crystal growth of the InAs-GaAs system.

We improved the graded solute concentration method by adopting an idea of partial melting. The partial melting is possible by heating the feed with preinstalled solute concentration gradient at a low temperature gradient as is shown in Fig. 3b: the high InAs concentration part has low melting temperature and is melted, while the low InAs concentration part has high melting temperature and remains unmelted. This method is different from a so-called zone melting method in which a steep temperature gradient is used to form a narrow melt zone as is shown in Fig. 3a. Figure 4 shows four steps of crystal growth by the concentration gradient partial melting method. A narrow melt zone is translated by the combination of lowering the ampoule in the vertical Bridgmann furnace and diffusion of InAs into the solid part of the feed. In this method, the apparent diffusion coefficient is smaller than the case of entire melting of the feed because diffusion rate is controlled by the dissolving rate

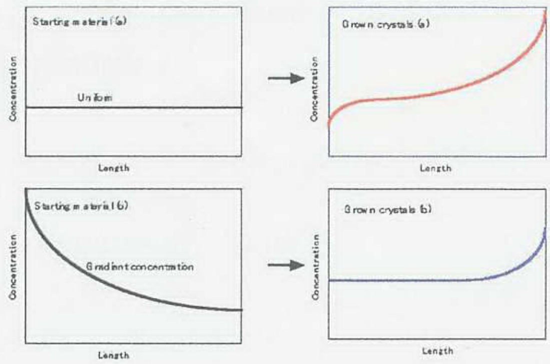
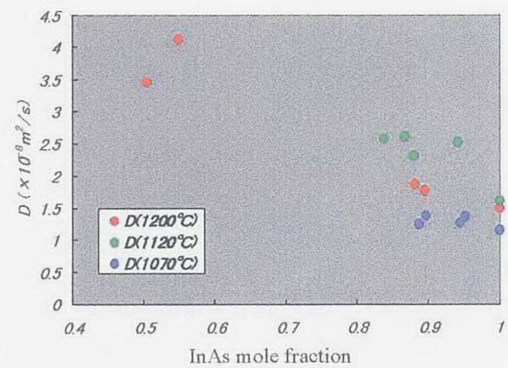
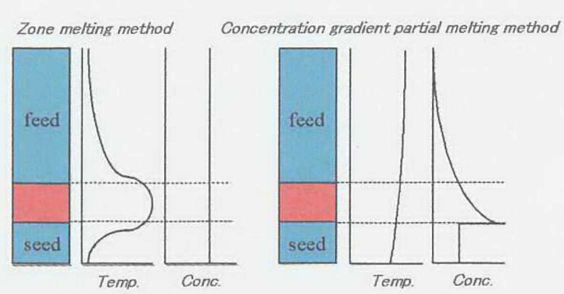


Fig. 1 Principle of the graded solute concentration method



InAs-GaAs interdiffusion coefficients

Fig. 2 InAs-GaAs interdiffusion coefficients.



Comparison of zone melting method and concentration gradient partial melting method

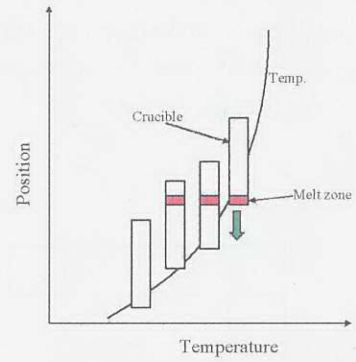
Fig. 3 Comparison of the zone melting method and the concentration gradient partial melting method.

of solid. Therefore, it is easier to control the solute concentration at C_0/k at the S/L interface (C_0: solute concentration in the original melt, k: segregation coefficient). The initial solute concentration can be controlled by adjusting both of the soaking period and a setting temperature at the beginning of crystal growth. In such a narrow melt zone, residual accelerations on the order of 10^{-4} G will not cause convective mixing and compositional variations due to residual accelerations will be suppressed, resulting in a homogeneous crystal growth. We simulated microgravity environments by growing crystals in capillary tubes (1.6 – 2.0 mm bores) because driving force for convection is suppressed in such capillary tubes even on the ground. We also grew crystals having 20 mm diameter for investigating effects of gravity. The nominal composition of the starting material was $In_{0.3}Ga_{0.7}As$. Feeds were prepared as follows: first, the starting material was inserted into a born nitride crucible and the crucible was sealed in a quartz ampoule at 1x 10^{-4} Pa. The ampoule was then heated in a vertical Bridgmann furnace at a temperature gradient of about 40°C/cm. After the starting material was entirely melted, the ampoule was translated at 1 mm/h toward the lower position and the melt was directionally solidified. The concentration profile was similar to that obtained by normal freezing of a melt. Thus prepared sample was used as a feed by inverting the position, namely the last to freeze end was set at the top in the crystal growth. Preparation procedures of feeds are presented in this conference in more detail[8].

3. Results and Discussion

Figure 5 shows an example of the compositional profile of the grown crystal. Crystal diameter is 1.6 mm. At the beginning of the growth, the temperature of the tip of the ampoule was set at 1060°C, and the ampoule was lowered at a rate of 0.5 mm/h after 3 h soaking. Temperature gradient in the furnace was about 25°C/cm. Note that more than 80% of the grown crystal is homogeneous with $x = 0.2 \pm 0.03$ in $In_xGa_{1-x}As$.

Figure 6 is another example of the compositional profile of the grown crystal.



Crystal growth by the concentration gradient partial melting method

Fig. 4 Schematic diagram of the concentration gradient partial melting method.

Crystal diameter is 2.0 mm in this case and the cross sectional view of the crystal along the growth axis is shown together with the compositional profile. In this case, a homogeneous part extends to a distance of longer than 35 mm and a single crystalline grain longer than 20 mm is observed, although no seed was used. The seed preparation has been carried out by one of the members and is presented in this conference [9]. Starting from feeds with nominal composition of $In_{0.3}Ga_{0.7}As$, we also succeeded in the single crystal growth with x = 0.3 and x = 0.33 having longer than 30 mm homogeneous parts and longer than 10 mm single grains with 2.0 mm diameter.

These results show the validity of the concentration gradient partial melting method for obtaining homogenous mixed crystals. The problem of residual acceleration in a melt in microgravity is solved by this method because homogeneous single crystals were grown by this method.

Then, we tried growth of large diameter crystals on the ground. The compositional profile of the 20 mm diameter crystal is shown in Fig. 7. Although InAs mole fraction is about 0.15 and the grown crystal is polycrystalline, homogeneous part is about 40 mm long, showing the validity of the method for obtaining homogeneous crystals. The problem to be settled is single crystallization of large diameter crystals. We should make clear what causes polycrystallization of large diameter crystals.

We think that convection in the melt causes polycrystallization and we expect that growth in microgravity will produce homogeneous large single crystals of $In_{0.3}Ga_{0.7}As$.

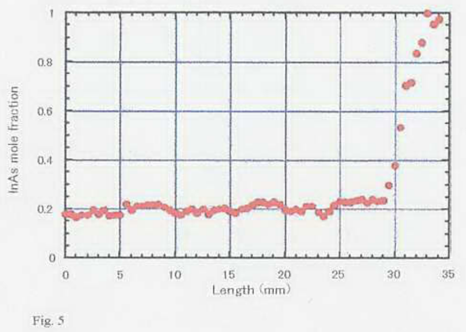


Fig. 5 Conentration profile showing homogeneous crystal growth with x = 0.2.

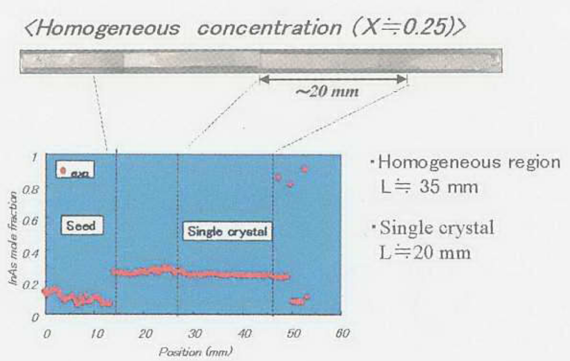


Fig. 6 Concentration profile showing homogeneous crystal growth with x = 0.25.

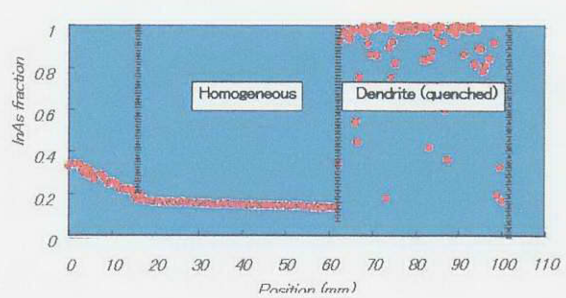


Fig. 7 Concentration profile showing homogeneous crystal growth with x = 0.15 and 20 mm in diameter.

4. Summary

We have developed the concentration gradient partial melting method for obtaining homogeneous mixed crystals by avoiding effects of convection due to residual acceleration in microgravity. Homogeneous crystals of $In_xGa_{1-x}As$ with x = 0.2 to 0.33 and diameters from 1.6 to 2.0 mm were successfully grown by this method on the ground. For further development of the method, single crystallization of large diameter crystals is being studied.

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