$In_{0.3}Ga_{0.7}As$ Seed Crystal Preparation Using The Multi-Component Zone Melting Method (II)

S. Kodama[†] **and T. Nakamura**[†]
K. Kinoshita[††], **H. Kato**[††], **and S. Yoda**[††]

† Fujitsu Laboratories Ltd., 10-1 Morinosato-wakamiya, Atsugi 243-0197, Japan
† † National Space Development Agency of Japan, Sengen 2-1-1, Tsukuba 305-8505, Japan

$In_{0.3}Ga_{0.7}As$ seed crystal preparation using the multi-component zone melting method is currently under way for space experiments. In a sample configuration with an InAs crystal sandwiched between GaAs seed and feed crystals, the x-value of growing $In_xGa_{1-x}As$ crystal is increased from 0.03 to 0.3 before maintaining at 0.3 for several millimeters of growth. As this year has progressed, we have increased the length of single crystalline $In_{0.3}Ga_{0.7}As$ from 4 to 6 mm, reduced scattering of the x-value in a $In_{0.3}Ga_{0.7}As$ layer from ± 0.01 to ± 0.005, and increased length of poly-crystalline $In_{0.3}Ga_{0.7}As$ from 18 to 20 mm. Since the required length of seed crystals in space experiments is 20 mm, the length of the single crystalline $In_{0.3}Ga_{0.7}As$ has to be increased.

1. Introduction

Ternary compound semiconductor bulk crystals such as InGaAs and InGaP are promising materials as substrates for high efficiency devices since the tunable lattice constant of such substrates enables design flexibility. This is unavailable with binary substrates. Infrared laser diodes (LDs) fabricated on $In_{0.31}Ga_{0.69}As$ substrates showed laser oscillations at 1.3 μm in wavelength and improved temperature characteristics beyond that of 1.3 μm LDs fabricated on InP substrates [1], as predicted theoretically [2]. However, the threshold current to initiate laser oscillations of LDs fabricated on $In_{0.31}Ga_{0.69}As$ substrates was much higher than that of LDs fabricated on $In_{0.22}Ga_{0.78}As$ substrates. This difference was attributed to the poorer crystal quality of $In_{0.31}Ga_{0.69}As$ substrates, as seen in wider full-width at half maximum of X-ray rocking curves. Therefore, high quality $In_{0.3}Ga_{0.7}As$ bulk crystals are desirable achieving high performance LDs emitting at 1.3 μm, which are desired for use as a light source in future optical access systems [2].

Growth of InGaAs bulk crystal has been tried using the cooling liquid encapsulated Czochralski (LEC) method [3], the Bridgman method [4], the vertical gradient freeze (VGF) method [5], the multi-component zone melting (MCZM) method [6-8], and the two-step MCZM method [9]. So far, only MCZM-related growth methods have enabled the growth of homogeneous $In_{0.3}Ga_{0.7}As$ single crystals. Because as the InAs composition increases, variations in the composition of the solidifying material become more sensitive to temperature fluctuations, as is known from the InAs-GaAs quasi-binary phase diagram. This leads to compositional inhomogeneity and initiation of poly-crystalline growth. The MCZM method enables the reduction of temperature fluctuations caused by buoyancy and convection by reducing the liquid volume. Therefore, we adopted the two-step MCZM method in the preparation of $In_{0.3}Ga_{0.7}As$ seed crystals.

Research over the past year [10] has revealed the following results. (1) Composition in growing crystal is controllable with the use of a sample travelling rate or furnace temperature control or both. As growth proceeds, the growth interface moves upward where the furnace temperature is higher because of the temperature gradient of the furnace. To grow a layer that has an increasing InAs composition, the sample has to be traveled at a higher rate than the growth rate to decrease the growth temperature or the furnace temperature has to be decreased as in the VGF method. To grow a homogeneous composition layer the sample has to be traveled at the same rate as the growth rate, or the furnace temperature has to be decreased at a specific rate to keep the growth temperature constant. (2) Single crystalline $In_{0.05}Ga_{0.95}As$ grows, while poly crystalline $In_{0.1}Ga_{0.9}As$ grows on GaAs seed crystals. Then, $In_xGa_{1-x}As$ where x is between 0.25 and 0.35 seed crystals are required to grow single crystalline $In_{0.3}Ga_{0.7}As$. (3) Single crystalline $In_{0.3}Ga_{0.7}As$ can be grown on GaAs seed crystals using the two-step MCZM method. In step one, $In_xGa_{1-x}As$ that has an InAs content increasing from 0.05 to 0.3 was grown on GaAs seed under decreasing furnace temperatures, as in the VGF method; then, in step two, homogeneous $In_{0.3}Ga_{0.7}As$ was grown under a constant growth temperature.

Last year, single crystalline $In_xGa_{1-x}As$ crystals grown using the above method were 15 mm in diameter and 28 mm in length, and the x-value was maintained at 0.34 ±0.01 in last grown region of 4 mm in length. This year, we made efforts toward achieving a longer $In_{0.3}Ga_{0.7}As$ region, a longer $In_{0.3}Ga_{0.7}As$ single crystalline region, and higher homogeneity.

2. Experiment

Figure 1 shows the sample setup and the principle of the two-step MCZM method. An InAs poly-crystal is sandwiched between a GaAs seed crystal and GaAs feed crystal. Next, this sample is inserted into a crucible, sealed in a quartz ampoule under high vacuum, and then processed in a vertical gradient heating furnace with the seed at the bottom. At temperatures exceeding 942°C (the mp. of InAs), the surfaces of the GaAs crystals next to the InAs dissolve into the InAs melt, and a ternary melt is formed. As is known from the InAs-GaAs pseudo-binary phase diagram, the GaAs composition near the feed region becomes denser than that near the seed region because of a temperature difference. This difference in composition causes GaAs to diffuse toward the seed crystal, resulting in excess GaAs composition on the growth interface and ternary crystal growth on the surface of the seed crystal. The ternary composition of the grown crystal is determined, in principle, by the temperature at the growth interface.

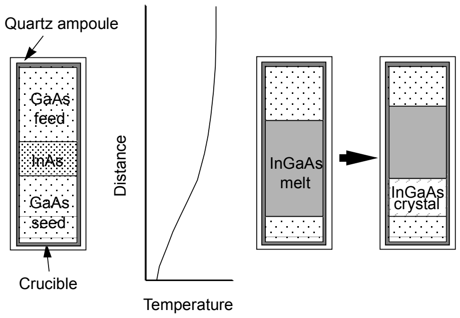


Fig. 1 Sample setup and principle of multi-component zone melting method.

All of the seed Si-doped GaAs crystals, feed Si-doped GaAs crystals, and the undoped InAs poly-crystals were cylindrical with a diameter of 15 mm, and the crystals had a typical length of 20, 20, and 10 mm, respectively. The seed is (111)B oriented. The crystals were set in a 15 mm diameter pyrolytic boron nitride or sandblasted quartz crucible and then sealed in a quartz ampoule in a vacuum of less than 8 x 10^{-5} Pa.

The sample was placed with the seed on the bottom in a vertical gradient heating furnace. After annealing at 930°C, the temperature at the growth interface was increased to the growth temperature, keeping the temperature gradient of the furnace constant. Crystal growth was carried out in two steps. (1) As the sample moved downward, the furnace temperature was gradually reduced to increase the InAs content of the growing crystal. (2) As the sample moved downward at the same rate as the growth rate, the furnace temperature and temperature gradient were kept constant to maintain a constant temperature at the growth interface, thereby keeping the InAs content of the growing crystal constant.

After growth, the crystals were cut along the growth direction and mechanically polished. Chemical etching was then done with $HF:HNO_3:H_2O$ = 1:2:2 to remove surface damage for evaluation purposes. Compositional variations in the grown layers were determined by energy dispersive X-ray (EDX) analysis. X-ray diffraction measurements were performed on the chemically treated wafers that were cut perpendicular to the growth direction.

3. Results and Discussion

3.1 Extension of $In_{0.3}Ga_{0.7}As$ region length

When we use GaAs feed, growth of $In_xGa_{1-x}As$ is limited to a certain length. During growth using the MCZM method, growth of the $In_{0.3}Ga_{0.7}As$ crystal on a seed crystal from the $In_{0.83}Ga_{0.17}As$ melt causes GaAs depletion in the melt. Dissolution of the feed material put at the hotter side of the melt compensates for this depletion. When using $In_{0.3}Ga_{0.7}As$ feed, we expect the volume of the melt to remain constant during growth since the consumption of elements at the growth interface is offset by the supply of elements as a result of the dissolution of feed material. However, when we use a GaAs feed, a lack of InAs component supply causes the volume of the InGaAs melt to decrease as growth proceeds. Finally, as the melt disappears, the growth terminates. Hence, the use of $In_{0.3}Ga_{0.7}As$ feed materials is better for growing longer homogeneous crystals, but formed material to make up the MCZM sample configuration is not yet available.

In this study, we simply increased the length of InAs poly-crystals from 10 to 18 mm and the length of GaAs feed crystals from 20 to 25 mm. Consequently, we achieved the growth of a poly-crystalline $In_{0.3}Ga_{0.7}As$ of 20 mm in length. However, the use of $In_{0.3}Ga_{0.7}As$ feed is preferable to grow longer single crystalline $In_{0.3}Ga_{0.7}As$ since increased melt volume in this method is sensitive to gravity, which causes convection in the melt.

3.2 Growth of $In_{0.3}Ga_{0.7}As$ single crystal and increment of homogeneity

Figure 2 shows the furnace temperature program. The temperature gradient of the furnace near the growth interface was 10°C/cm. The sample was pulled downward at a rate of 0.1 mm/h, which is the minimum rate of the apparatus, during the entire experiment. The furnace temperature was raised to 1170°C and maintained at that temperature for one hour for seeding. Next, the furnace was gradually cooled to 1000°C to increase the InAs content in the growing crystal, and then increased to 1010°C at a rate of 0.05°C/h for 200 hours to grow homogeneous $In_{0.3}Ga_{0.7}As$ crystal. The final temperature increase compensates for differences between the growth rate and sample traveling rate. A growth rate lower than the sample traveling rate causes interface movement to the colder side of the furnace, thereby increasing InAs composition in the growing crystal, as seen in Fig. 5 in Ref. 10.

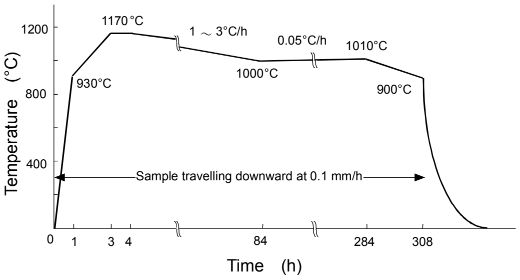


Fig. 2 Temperature-time profile of the furnace

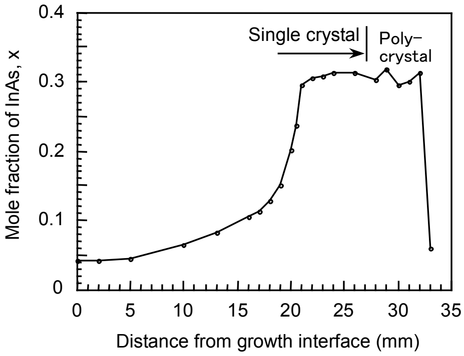
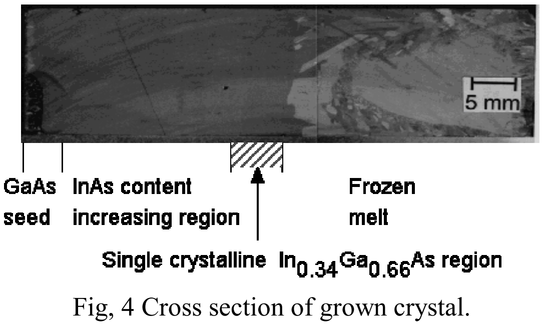


Fig. 3 Compositional variation in growth direction of crystal grown using furnace temperature program shown in Fig. 2.



Fig, 4 Cross section of grown crystal.

Figure 3 shows the compositional variation in the growth direction, and Fig. 4 shows a cross section of the grown crystal. Meltback of the GaAs seed crystal was 15 mm in depth. The InAs content of the growing crystal increases monotonically from an initial value of 0.04 to 0.3 during a growth of 22 mm in length. During a further growth of 6 mm in length, the InAs content was maintained at 0.309 ±0.005 due to growth temperature compensation. Figure 4 shows that we successfully accomplished single crystal growth in this step. Afterward, a multi-grain region grew during the cool down to room temperature.

3.3 Evaluation of crystal quality

We made an evaluation using the X-ray diffraction measurements from the $In_xGa_{1-x}As$ crystal grown last year. Figure 5 shows the Cu $K_{\alpha 1}$ X-ray rocking curves for the (111) reflections of (a) a GaAs wafer and (b), (c), (d) the grown InGaAs bulk crystal. The Si (111) diffracted incident beam was 0.5 mm in diameter. Rocking curves (b), (c), and (d) were measured at 19, 24, and 28 mm, respectively, from the initial growth interface. The diffraction intensity of the InGaAs crystals was weaker than that of the GaAs wafer, and the half-width of the diffraction peak for the InGaAs crystals was wider than that of the GaAs wafer. Furthermore, the half-width of the $In_{0.3}Ga_{0.7}As$ region was wider than that of the $In_{0.14}Ga_{0.86}As$ crystal. Since the half-width remained in this region of 4 mm in length for about 2 minutes, we can say that a relatively good $In_{0.3}Ga_{0.7}As$ bulk crystal of 4 mm in length was grown.

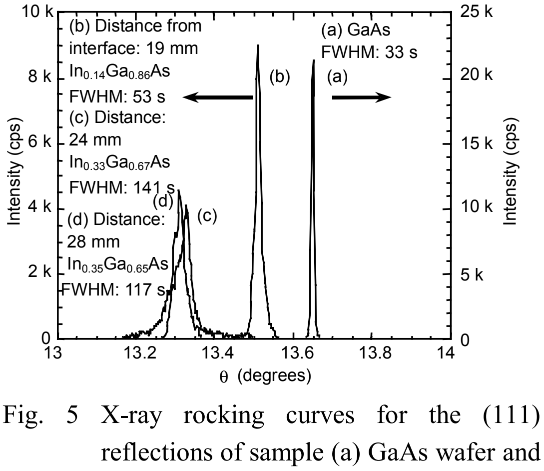


Fig. 5 X-ray rocking curves for the (111) reflections of sample (a) GaAs wafer and (b)-(d) grown InGaAs bulk crystal at several distances from the initial growth interface.

4. Summary

A 28 mm long single crystalline $In_xGa_{1-x}As$ ternary bulk crystal was grown on a GaAs seed crystal using the two-step MCZM method. The InAs composition of grown crystal was gradually increased from 0.04 at the initial growth interface to 0.3, and the composition of the subsequent 6 mm long growth was maintained at 0.309 ±0.005. So far, the single-crystalline length of $In_{0.3}Ga_{0.7}As$ is limited to 6 mm. However, growth of poly-crystalline $In_{0.3}Ga_{0.7}As$ of 20 mm in length has been carried out. Therefore, the use of this method seems promising for achieving longer $In_{0.3}Ga_{0.7}As$ single crystals in demand as seed crystals in space experiments.

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