$In_{0.3}Ga_{0.7}As$ Seed Crystal Preparation using the Multi-Component Zone Melting Method

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$In_{0.3}Ga_{0.7}As$ seed crystal preparation using the multi-component zone melting method is currently under way for space experiments. A 28 mm long single crystalline $In_xGa_{1-x}As$ ternary bulk crystal has been grown on GaAs seed crystal so far. The InAs composition of the grown crystal was gradually increased from 0.04 at the initial growth interface to 0.33 by decreasing the growth temperature, as in the vertical gradient freeze method. Then the composition was maintained at 0.34 ±0.1 during a growth of 4 mm in length by moving the sample at a rate nearly equal to the growth rate. The required length of seed crystals for space experiments is 20 mm. So the length of the homogeneous region has to be increased.

1. Introduction

Ternary compound semiconductor bulk crystals such as InGaAs and InGaP are promising materials to be used 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 fabricated on $In_{0.22}Ga_{0.78}As$ substrates showed laser oscillations at 1.22 μm in wavelength and improved temperature characteristics[1]. InGaAs bulk crystals with a higher In content are desired because the use of $In_{0.3}Ga_{0.7}As$ substrates allows the fabrication of high performance lasers 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 several methods. Bonner et al. [3] used the cooling liquid encapsulated Czochralski (LEC) method and grew InGaAs crystals with an InAs composition varying from 0.05 to 0.12. Nishijima et al. [4] used a vertical gradient freeze (VGF) method and grew InGaAs single crystals with an InAs composition varying from 0.05 to 0.3. Using the multi-component zone melting (MCZM) method Suzuki et al. [5] grew compositionally graded InGaAs single crystals without sample movement, and Nakajima and Kusunoki [6] grew homogeneous poly-crystalline $In_{0.3}Ga_{0.7}As$ with sample movement or gradual cooling. As the InAs composition increases, the variation in the composition of the solidifying material becomes more sensitive to temperature fluctuation, 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 allows the reduction of temperature fluctuations caused by buoyancy and convection by reducing the liquid volume. So we adopted the MCZM method for preparation of $In_{0.3}Ga_{0.7}As$ seed crystals.

2. Experiment

Figure 1 shows the sample setup and the principle of the MCZM method. An InAs poly-crystal is sandwiched between a GaAs seed crystal and a GaAs feed crystal. This sample is then 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

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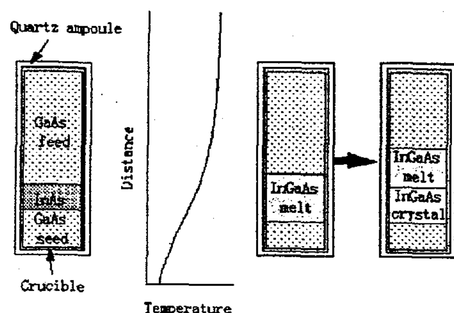

Fig.1 Sample setup and principle of the multi-component zone melting method.

GaAs composition near the feed region becomes denser than that near the seed region because of the 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.

The seed and feed Si-doped GaAs crystals and the undoped InAs poly-crystal were all cylindrical with a diameter of 15 mm, and had typical lengths 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 crucible and then sealed in a quartz ampoule in a vacuum of under 8 x 10^{-5} Pa.

The sample was set in a vertical gradient heating furnace with the seed placed at the bottom. 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 by simply maintaining the temperature gradient or by moving the sample downward, for evaluation of the MCZM method. For attempts to grow $In_{0.3}Ga_{0.7}As$ crystals on GaAs seed crystals, growth was carried out in two steps: (1) Moving the sample downward and reducing the furnace temperature gradually to increase the InAs content of the growing crystal. (2) Moving the sample downward at the same rate as the growth rate while keeping the furnace temperature and temperature gradient 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. Then chemical etching was done with H_2SO_4:H_2O_2:H_2O = 90:5:5 to remove surface damage for evaluation purposes. The compositional variations in the grown layers were determined by energy dispersive X-ray (EDX) analysis.

3. Results and Discussion

3.1 Basic evaluations on the MCZM method

Figure 2 shows the compositional variations in the growth direction in grown layers with (a) an initial growth temperature of 1070°C, without sample movement, (b) an initial growth temperature of 1085°C, and a sample traveling rate of 0.15 mm/h, and (c) an initial growth temperature of 1110°C, and a sample traveling rate of 0.5 mm/h. The temperature gradient of the furnace was 20°C/cm. Initial growth compositions were determined by the initial growth temperatures. As growth proceeds, the growth interface moves upward. When the sample is kept stationary, the growth temperature increases because of the temperature gradient of the furnace. This temperature increase results in a decrease of the InAs composition as indicated by the phase diagram (a) (the same result as in Ref. 5). When the sample traveling rate mirrors the growth rate, the growth temperature is kept constant resulting in homogeneous crystal growth (b) (the same result as Ref. 6). When the sample traveling rate is higher than the growth rate, a decrease in growth temperature increases the InAs composition (c). These experimental results reveal that the composition along the growth direction is controllable by the sample traveling rate.

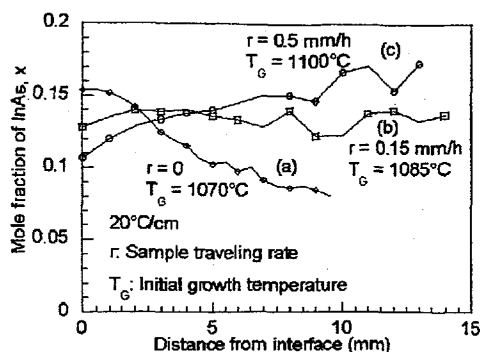

Fig.2 Compositional variations in the growth direction of grown layers.

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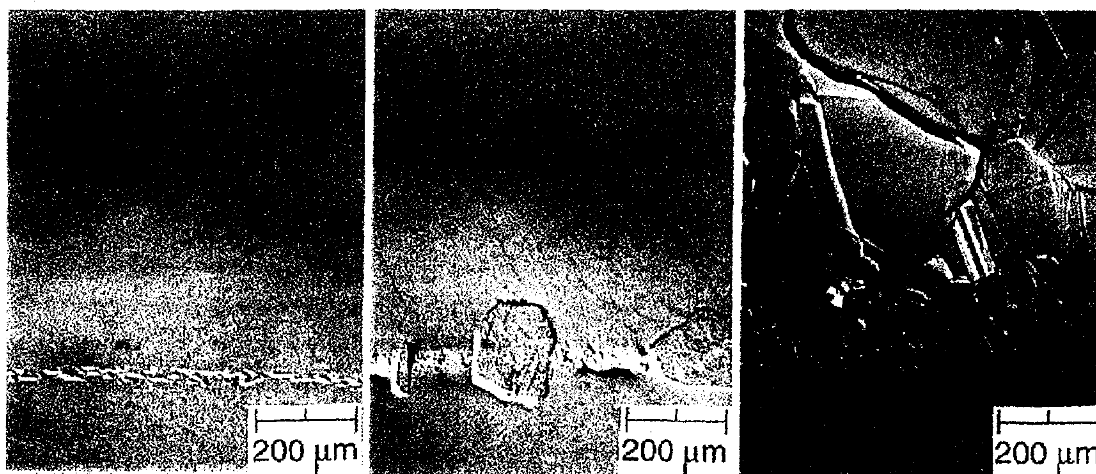

Fig.3 AB etched cross sections of (a) $In_{0.05}Ga_{0.95}As$, (b) $In_{0.1}Ga_{0.9}As$, (c) $In_{0.15}Ga_{0.85}As$ crystals grown on GaAs. The lattice mismatches $\Delta a/a$ are 0.4, 0.7, and 1.1 %, respectively.

Figure 3 shows the AB etched [7] cross sections of (a) $In_{0.05}Ga_{0.95}As$, (b) $In_{0.1}Ga_{0.9}As$, and (c) $In_{0.15}Ga_{0.85}As$ crystals grown on GaAs. The initial growth temperatures were 1180, 1120, and 1085°C, respectively. The lattice constant of $In_xGa_{1-x}As$ crystal varies drastically from 5.65 Å to 6.06 Å with an x variation from 0 to 1. When the lattice mismatch between the seed crystal and growing crystal is small (a, $\Delta a/a$ = 0.4 %), the growth interface is a bit smeared, but the growth is continuous. In the case of x=0.1 (b, $\Delta a/a$ = 0.7 %), sub grains appear at the growth interface, and dislocations are introduced in the grown crystal. Further mismatch causes poly crystal growth from the interface (c, $\Delta a/a$ = 1.1 %). Then, we may say that single crystalline $In_xGa_{1-x}As$ may grow on $In_yGa_{1-y}As$ seed crystals where y is between x - 0.05 and x + 0.05.

3.2 Attempt to grow $In_{0.3}Ga_{0.7}As$ seed crystals

We selected GaAs crystal as a starting seed material because high quality crystals are available. Then the initial growth temperature of 1180°C was selected to make the InAs content of the first growing crystal less than 0.05. To increase the InAs content of the growing crystal, the furnace temperature was reduced gradually as in the VGF method. Fig 4 shows the furnace temperature program. The temperature gradient of the furnace was 40°C/cm. The sample was pulled downward at the rate of 0.1 mm/h, which is the minimum rate of the apparatus, during whole of the experiment. The furnace temperature was raised to 1180°C, and maintained at that temperature for one hour for seeding. Actually initial growth of about 0.1 mm in thickness occurred during this period due to the transportation of GaAs from the hotter feed region to the cooler seed region. Then the furnace was cooled gradually to 995°C, to increase the InAs content in the growing crystal, and then held at this temperature for 80 hours to grow homogeneous $In_{0.3}Ga_{0.7}As$ crystal.

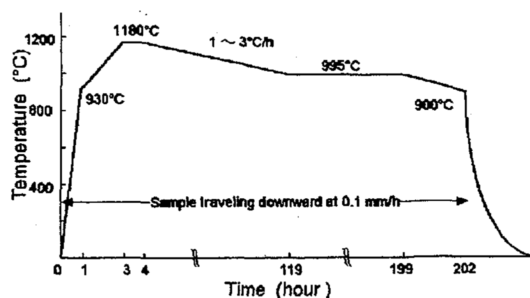

Fig.4 Furnace temperature program for an attempt to grow $In_xGa_{1-x}As$ crystal in which x increases from 0.04 to 0.3 and after that remains constant at 0.3 on GaAs seed crystal.

Fig. 5 shows the compositional variation in the growth direction, and Fig. 6 shows a cross section of the grown crystal. Meltback of the GaAs seed crystal was 16 mm in depth. The InAs content of the growing crystal increases monotonically from

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the initial value of 0.04 to 0.33 during a growth of 24 mm in length. Further growth of a 4 mm length caused the InAs content to increase to 0.35. As shown in Fig. 6 we succeeded in making single crystal growth until this step. After that, a multi-grain region grew during the cool down to room temperature. The length of the homogeneous region was 4 mm for 80 hours growth. So the growth rate of this condition was estimated to be 0.05 mm/h. Then the difference between the sample travelling rate of 0.1 mm/h and the growth rate of 0.05 mm/h caused growth interface movement downward thereby decreasing the growth temperature and increasing the InAs content in the grown layer. This problem of increasing InAs content in growing crystal will be solved by increasing the growth rate, by decreasing the sample traveling rate, or by compensating temperature decrease at the growth interface by increasing the furnace temperature at a certain rate.

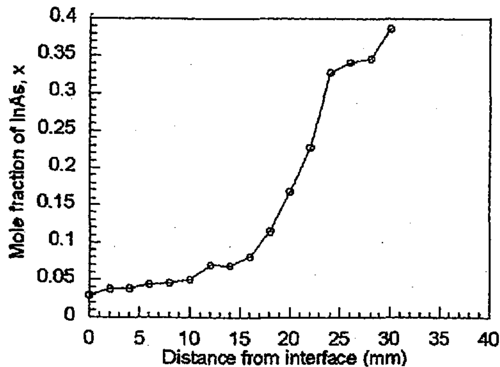

Fig.5 Compositional variation in the growth direction of the crystal grown using the furnace temperature program shown in Fig.4

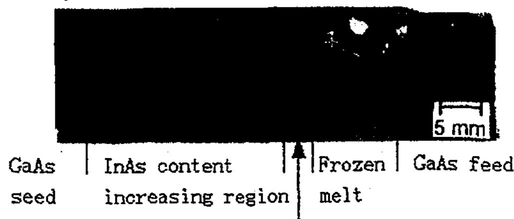

Fig.6 Cross section of the grown crystal.

Conclusion

A 28 mm long single crystalline $In_xGa_{1-x}As$ ternary bulk crystal was grown on GaAs seed crystal using the two step MCZM method, decreasing the furnace temperature to increase InAs content in growing crystal as in the VGF method and keeping the growth temperature constant to grow homogeneous crystal. The InAs composition of grown crystal was gradually increased from 0.04 at the initial growth interface to 0.33, and that of the following 4 mm length of growth was kept at 0.34 ± 0.01.

The specifications of the seed crystals for space experiments are single crystalline, 5 mm in diameter, 20 mm in length, and an $In_{0.3}Ga_{0.7}As$ homogeneous region length of at least 15 mm. Thus more improvement has to be done for seed crystal preparation.

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