$In_{0.3}Ga_{0.7}As$ SEED CRYSTAL PREPARATION USING THE MULTI-COMPONENT ZONE MELTING METHOD (III)

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Abstract

$In_{0.3}Ga_{0.7}As$ 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 was increased from 0.04 to 0.3 before being maintained at 0.3 for several millimeters of growth. Efforts to increase the single crystalline growth yield have been carried out this year. The appearance of poly-crystallization in the initial stages, during the stage of increasing InAs composition, and during the constant-composition growth stage were studied. Measures were taken to prevent poly-crystalline growth. The yield of single-crystalline structures was thus increased from 0.05 to 0.5. We have used these improved conditions of growth to prepare ten seed crystals for ground experiments.

1. Introduction

Ternary compound semiconductor bulk crystals such as InGaAs and InGaP are promising materials for use as the substrates for high efficiency devices since the tunable lattice constant of such substrates enables design flexibility. This feature is not available with binary substrates. Infrared laser diodes (LDs) fabricated on $In_{0.31}Ga_{0.69}As$ substrates have produced laser oscillations at a wave length of 1.3 μm and have demonstrated improved temperature characteristics beyond those of 1.3 μm LDs fabricated on InP substrates [1], as predicted theoretically [2].

Several methods for growing InGaAs bulk crystal have been tried [3-9]. So far, the growth of homogeneous single crystals of $In_{0.3}Ga_{0.7}As$ has only been possible with methods based on the multi-component zone melting (MCZM) method. We have developed a two-step MCZM method and used it to grow a 28 mm long single-crystalline $In_xGa_{1-x}As$ ternary bulk crystal on a GaAs seed crystal. 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 growth of 6 mm was maintained at 0.309 ±0.005. The single-crystalline growth yield was, however, only about 0.05 (once in 20 trials). To provide a supply of seed crystals for use in space and ground experiments, a higher yield was essential.

2. Experimental

The sample setup and principle of the two-step MCZM method are reported in the literature [9-11]. An InAs poly-crystal is sandwiched between a GaAs seed crystal and a GaAs feed crystal. Next, this sample is placed in 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. Fig. 1 shows a typical temperature-time profile of a growth experiment. At temperatures above 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 thus formed. The temperature at the growth interface is then increased to the temperature of growth, while maintaining a constant temperature gradient in the furnace. As is known from the InAs-GaAs pseudo-binary phase diagram, the GaAs composition near the feed region becomes richer than that near the seed region because of a temperature difference. This difference in composition causes GaAs to be diffused towards the seed crystal, and this creates an excessive proportion of GaAs at the growth interface and thus induces the growth of ternary crystal 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.

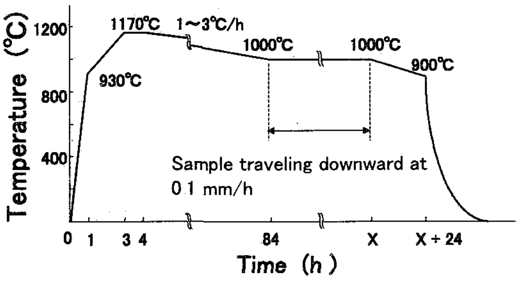

Fig. 1 A typical temperature-time profile of a growth experiments.

In our growth method, the crystal is grown in two steps; (1) a step in which the InAs composition is increased and (2) a step of growth with a constant InAs composition. (1) The sample was kept stationary, while the furnace temperature was gradually decreased, but faster than the temperature increase caused by the shift of the spontaneous growth interface shift towards the hotter side of the furnace, to increase the InAs content in the growing crystal. (2) The sample was translated downward at the same rate as the rate of spontaneous growth, with the furnace temperature and the temperature gradient kept constant to maintain a constant temperature at the growth interface, thereby maintaining a constant InAs composition in the growing crystal.

Here, we report on the results of an experimental investigation of single-crystal growth under these conditions.

3. Results and Discussion

The appearance of poly-crystallization was observed in (1) the seeding stage, (2) the stage of increasing InAs composition in the growing crystal, and (3) the stage of growth with a constant InAs composition.

3.1 Poly-crystallization in the seeding stage

Fig. 2 shows an A-B etched cross

section of a crystal poly-crystallinity appeared at the beginning of the growth. In the region indicated by the arrow, the In-Ga-As melt has penetrated into the gap between the outer surface of the seed crystal and the inner surface of the crucible in the seeding stage. The temperature of the seed was lower than the solidus temperature of the melt which has been penetrated. The melt then solidified rapidly and formed no epitaxial relationship with the seed crystal. The result was the appearance of poly-crystallization.

We use well-designed crucibles and seed crystals to solve this problem, keeping the clearance between the two materials to less than 0.1 mm.

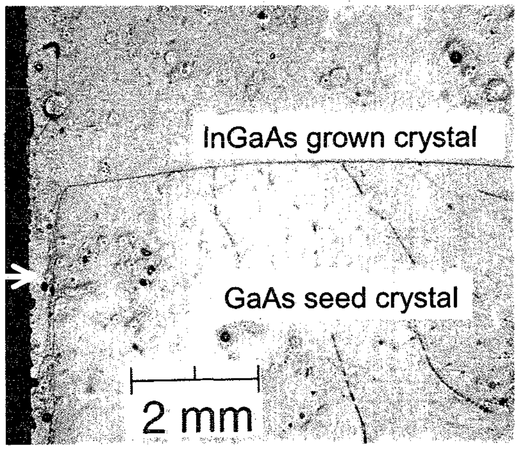

Fig. 2 A-B etched cross-section through a crystal that experienced poly-crystallization at the beginning of its growth.

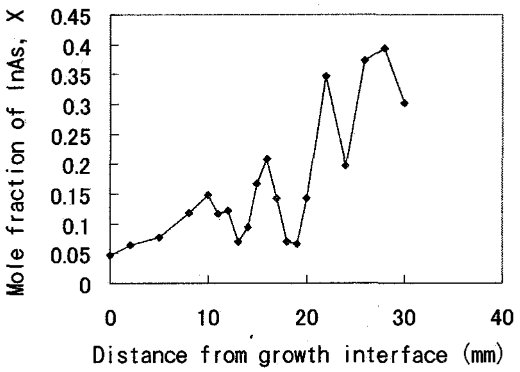

Fig. 3 InAs compositional variation along the growth direction of a poly-crystalline grown crystal using sintered BN crucible purified by baking in Nitrogen.

3.2 Poly-crystallization during the stage of increasing the InAs composition in the growing crystal

Fig. 3 shows an InAs compositional variation along the growth direction of a poly-crystalline grown crystal using sintered BN crucible, which had been purified by baking at 1000°C for 5 hours in an atmosphere of nitrogen. The InAs composition varies in a saw tooth pattern. These compositional fluctuations did not appear when we used a sintered BN crucible baked in a high vacuum or a pyrolytic BN crucible. We then concluded that this type of poly-crystallization is a result of the nucleation of InGaAs on impurity sites of the surface of the crucible in the early stages of growth. These nuclei grew, during the gradual cooling period, into larger crystals that were in orientations other than that of the seed crystal. We thus used a sintered BN crucible that had been baked in a high vacuum or a pyrolytic BN crucible to prepare our seed crystals.

Fig. 4 shows InAs compositional variation along the growth direction of a crystal that has become poly-crystalline in the third way. This type of poly-

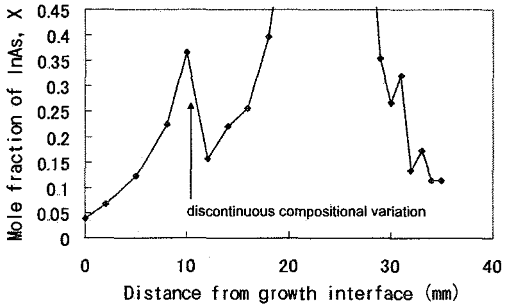

Fig. 4 InAs compositional variation along the growth direction of a crystal poly-crystallized because of constitutional super cooling during controlled cooling at the rate of 3℃/min in the early stages of growth.

crystallization may be characterized as a discontinuous compositional variation in the direction of growth. This was caused by constitutional super cooling during controlled cooling at a rate of 3°C/min in the early stages of growth. Detailed consideration of the condition of growth indicated that the G/R (temperature gradient/growth rate) value was nearly same as the $mC_L(1-k)/kD$ value, where m, C_L, k, and D are the gradient of the liquidus line, InAs composition in the bulk melt, coefficient of the distribution of InAs, and coefficient of the diffusion of InAs, respectively. To establish stable growth, the G/R value must be grater than $mC_L(1-k)/kD$. We then reduced the cooling rate to 1°C/min to decrease the growth rate, and succeeded in avoiding poly-crystallization of this type.

3.3 Poly-crystallization within a growing crystal

Fig. 5 shows cross sections of a grown crystal in which poly-crystallization has started within the crystal. According to measurements of photo-luminescence, there was a higher proportion of GaAs in these grains than in the surrounding single-crystalline region. The difference in composition reveals that these grains had started to grow in the melt before the growth interface had reached this region from the seed crystal. As growth proceeded, this grain was embedded in the structure as a whole. We consider these grains to have been induced by the growth of small crystals in the solution, from nuclei that were formed by constitutional supercooling or by some impurities in the melt, but are not certain on this point. Despite our lack of a theoretical solution to this problem, we were still able to prepare InGaAs seed crystals for use in ground experiments, since the probability of this type of poly-crystallization was less than 0.3.

3.4 Preparation of InGaAs seed crystals for use in ground experiments

We were able to prevent some mechanisms of poly-crystallization and thus, raise the single-crystalline growth yield from 0.05 to 0.5. We then used these growth conditions to prepare ten $In_{0.3}Ga_{0.7}As$ seed crystals for use in ground experiments.

(1) Crucible: Precisely manufactured pBN

(2) Clearance between crucible and GaAs seed crystal: < 0.1 mm

(3) Temperature setting of the furnace at the seeding stage:

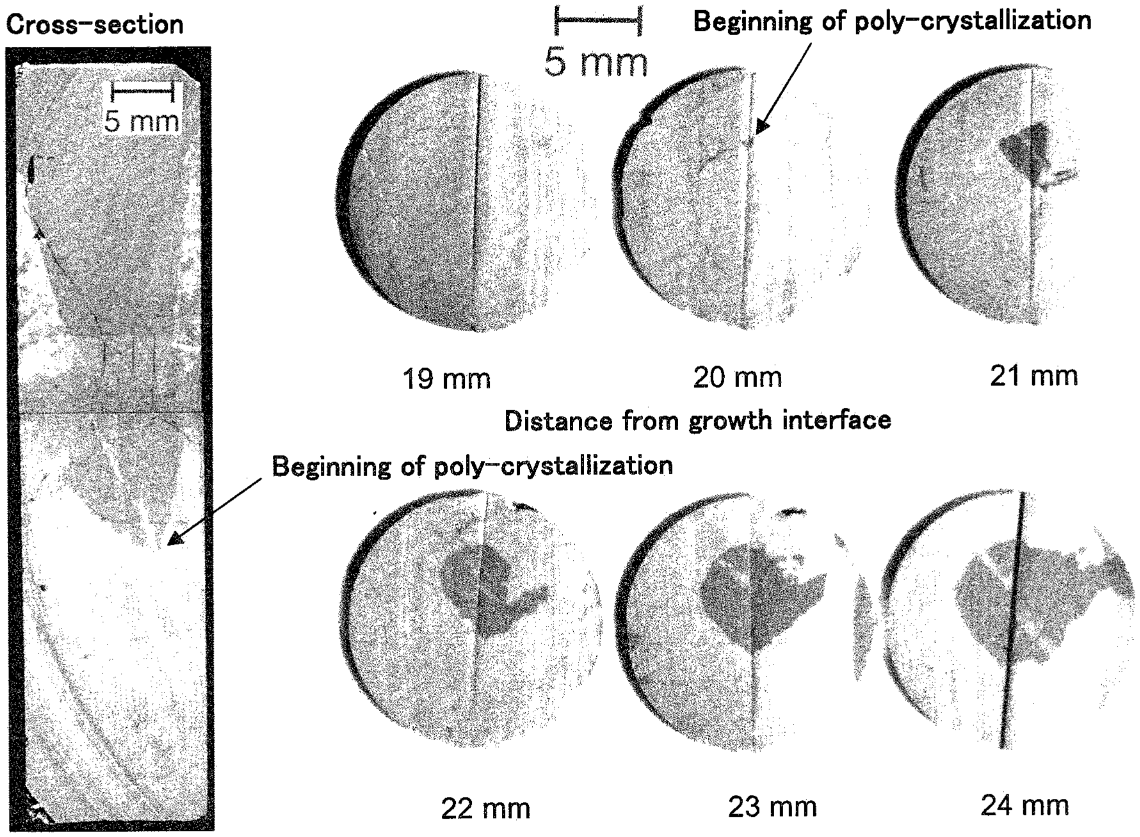

Fig. 5 Cross-sections through a grown crystal in which poly-crystallization has started within the crystal.

H1: 1170 - 1185℃

H2: 1125℃

H3: 700℃

(4) Rate of cooling during stage of increasing InAs composition: < 1℃/h

(5) Temperature gradient in the furnace: 3 - 7℃/cm

(6) Sample's rate of travel: 0.1 mm/h

Summary

We have investigated the appearance of poly-crystallization, during the growth of $In_{0.3}Ga_{0.7}As$ crystals. We were able to identify and prevent the mechanisms responsible for this phenomenon in the seeding stage and stage of growth with an increasing proportion of InAs. Finally, we found growth conditions which gave us a yield of 0.5 in growing single crystals of InGaAs. Under these conditions of growth, we prepared ten InGaAs seed crystals for use in ground experiments.

References

1) K. Otsubo, Y. Nishijima, T. Uchida, H. Shoji, K. Nakajima, and H. Ishikawa,. Jpn. J. Appl. Phys, **38** (1999) L312.

2) H. Ishikawa, Appl. Phys. Lett., **63** (1993) 712.

3) W. A. Bonner, B. J. Skromme, E. Berry, H. L. Gilchrist, and R. E. Nahory, Proc. 15th Intl. Symp. on GaAs and Related Compounds, Atlanta, GA, 1988, Inst. Phys. Conf. Ser. 96, ed. J. S. Harris (Bristol: Inst.

Phys., 1989) 337.

4) K. Nakajima, T. Kusunoki, and K. Otsubo, J. Crystal Growth, **173** (1997) 42.

5) Y. Nishijima, K. Nakajima, K. Otsubo, and H. Ishikawa, J. Crystal Growth, **197** (1999) 769.

6) T. Suzuki, K. Nakajima, T. Kusunoki, and T. Kato, J. of Electronic Mate., **25** (1996) 357.

7) K. Nakajima and T. Kusunoki, J. Crystal Growth, **169** (1996) 217.

8) Y. Nishijima, K. Nakajima, K. Otsubo, and H. Ishikawa, J. Crystal Growth, **208** (2000) 171.

9) S. Kodama, Y. Furumura, K. Kinoshita, H. Kato, and S. Yoda, J. Crystal Growth, **208** (2000) 165.

10) S. Kodama, Y. Furumura, K. Kinoshita, H. Kato, and S. Yoda, NASDA Technical Memorandum, **990006E** (1999) 57