Scaling up of TLZ-grown platy $In_{0.3}Ga_{0.7}As$ crystals for semiconductor laser substrates

By

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Abstract : We have succeeded in scaling up of platy $In_{0.1}Ga_{0.9}As$ single crystals grown by the traveling liquidus-zone (TLZ) method from 10 to 20 mm in width without deteriorating compositional uniformity. The TLZ method which we have invented for growing homogeneous mixed crystals requires diffusion-limited mass transport and convection in a melt should be avoided. In that point, large diameter crystals for substrate use were difficult to be grown on the ground because convection in a melt is intensified by the enlargement of diameter. Therefore, we attempted to grow platy $In_{1-x}Ga_xAs$ crystals. Merits of platy crystals are suppression of convection in a melt by limiting the thickness of the melt and achievement of sufficient area for substrate use. Successful scaling up of platy crystals shows that enlargement of the width of platy crystals will not affect the intensity of convection in a melt. This result supports the hypothesis that convection in a platy melt is limited by its small thickness and not by its width.

Key words : semiconductor, crystal growth, convection, substrate, laser diode

1. Introduction

$In_{0.3}Ga_{0.7}As$ is promising as a substrate of a laser diode operating at the wavelength of 1.3 μm used in the optical communication system. However, the growth of such ternary alloy crystals with uniform composition is not easy. This is mainly due to the fact that the liquidus and solidus curves are away too much and maintaining a constant interfacial composition during the growth process is extremely difficult. To overcome this problem, we have invented a new crystal growth method and named it the traveling liquidus-zone (TLZ) method based on the feature of the method [1-3]. The TLZ method requires diffusion limited mass transport and convection in a melt should be avoided. Homogeneous $In_{0.3}Ga_{0.7}As$ single crystals with length of longer than 20 mm have been grown when the crystal diameter is 2 mm since convection in a melt is suppressed in such capillary tubes even on the ground. However, large diameter crystals were difficult to be grown due to convection. Therefore, we attempted to grow platy $In_{0.3}Ga_{0.7}As$ crystals for substrate use and obtained homogeneous $In_{0.3}Ga_{0.7}As$ crystals with surface area of larger than $10\times20mm^2$ and 2mm in thickness [4]. This result implies that convection in a melt was sufficiently suppressed by limiting its thickness to 2 mm. If this is so, enlargement of the width of platy crystals is possible without deteriorating compositional homogeneity. In order to verify above hypothesis, we tried to enlarge the width of platy crystals from 10 to 20mm in the growth of $In_{0.1}Ga_{0.9}As$ by the TLZ method and obtained successful results. Here, we report on the results of our attempts.

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2. Principle of the TLZ method

Figure 1 explains the principle of the TLZ method by referring to the $In_{1-x}Ga_xAs$ crystal growth. The feature of the method is formation of a saturated solution zone (liquidus-zone) under the temperature gradient. Such zone is formed by heating a feed having stepwise or graded InAs concentration with excess InAs concentration in the seed side. Relations among temperature, zone position, concentration profile in a sample and the equilibrium phase diagram of the pseudobinary InAs-GaAs system are depicted in the figure. The unique point of the TLZ method is the spontaneous growth without sample cooling: the freezing interface travels spontaneously towards the lower InAs concentration side (higher temperature side) due to interdiffusion between InAs and GaAs in the zone. At the freezing interface, InAs is supplied by segregation on solidification. Therefore, spontaneous growth continues under the imposed temperature gradient. The driving force in the TLZ method is thus interdiffusion and segregation. When the sample device is translated in the opposite direction to the interface shift at the same rate of freezing, the interface is fixed at the same position relative to a furnace and the freezing temperature is kept constant. Then, the constant concentration of a growing crystal is achieved. Based on our one-dimensional model [2, 3], the spontaneous interface shift V is calculated as

$$V = -\frac{D}{C_{L0} - C_{S0}} \left(\frac{\partial C}{\partial T} \right) \left(\frac{\partial T}{\partial z} \right) \tag{1}$$

where D is the interdiffusion coefficient between InAs and GaAs, C_{L0} and C_{S0} are InAs concentration in a liquid and in a solid at the freezing interface, respectively. $\partial C/\partial T$ and $\partial T/\partial z$ are reciprocal of the slope of the liquidus and the temperature gradient at the freezing interface respectively and z is the distance measured from the freezing interface. The interdiffusion coefficient at about 1070℃ has been measured by using a sounding rocket [5]. Since C_{L0}, C_{S0} and $\partial C/\partial T$ are known from the phase diagram, V is calculated when the temperature gradient at the freezing interface $\partial T/\partial z$ is measured.

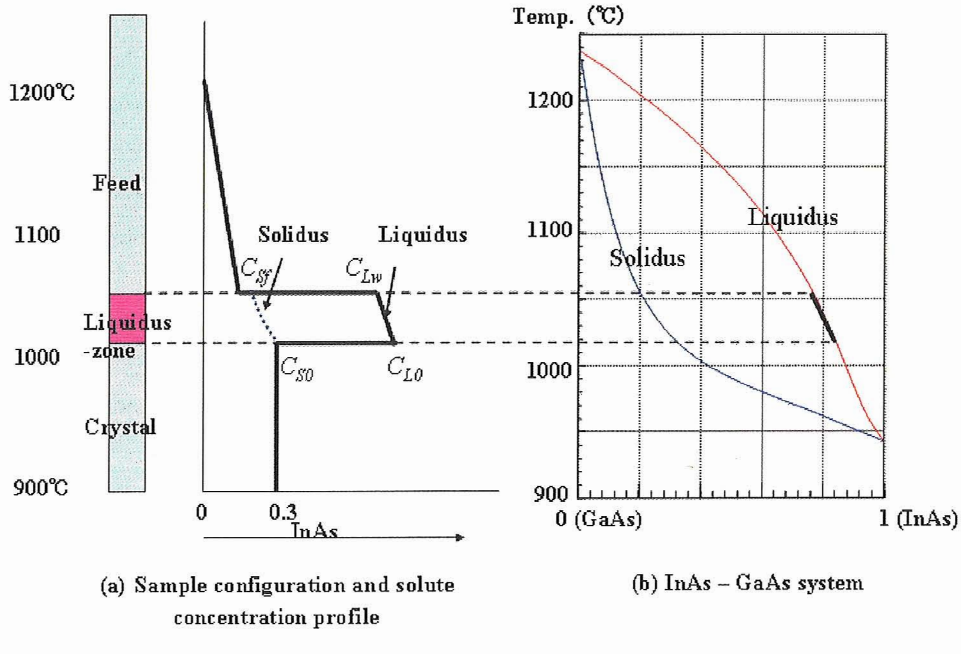


Fig. 1. Principle of the TLZ method referring to the InAs-GaAs system. Relation among temperature distribution, solute concentration, liquidus-zone and the equilibrium phase diagram of the system is shown.

Validity of our TLZ growth model was confirmed by the growth of 2 mm diameter crystals as reported previously [2-4] because homogeneous $In_{0.3}Ga_{0.7}As$ crystals were grown by the sample translation rate which was predicted by the eq. (1). The terrestrial 2 mm diameter crystal growth was aimed at suppression of convection in a melt during crystal growth, which is required for the TLZ growth.

3. Experimental

A GaAs seed, an InAs zone former, and a GaAs feed were cut into plates with 2 mm thickness and 10 or 20 mm width and these were inserted into a boron nitride crucible with a rectangular bore. The orientation of the seed was <100> with {100} surfaces perpendicular to the growth axis and the length of the feed was 40 or 50 mm. The crucible was then sealed in vacuum in a quartz ampoule at about 1×10^{-4} Pa. This ampoule was set in a temperature gradient furnace and was heated so that the interface temperature between the seed and the liquidus-zone was about 1120℃ for $In_{0.1}Ga_{0.9}As$ crystal growth. The highest temperature in the furnace was below 1190℃ so that the GaAs feed was not melted completely. The temperature gradient around 1120℃ was 20 - 30℃/cm. As the liquidus-zone travels to the lower In concentration side due to interdiffusion between InAs and GaAs (to the higher temperature side), the ampoule was translated towards the lower temperature side in order to maintain the same position relative to the furnace in accordance with the freezing rate of 0.36 mm/h as calculated by the equation (1) when the temperature gradient was 28℃/cm.. The grown crystal was first roughly polished and checked whether the grain boundary exists or not. Then, the crystal was mirror polished and compositional profiles were measured by using an electron probe micro-analyzer (EPMA). Crystal quality was evaluated by X-ray rocking curve measurements.

4. Results and discussion

First, 10 mm wide $In_{0.1}Ga_{0.9}As$ platy crystals were grown. Roughly polished surface of one of the grown crystals and InAs concentration profile along the growth axis are shown in Fig. 2 as a typical example.

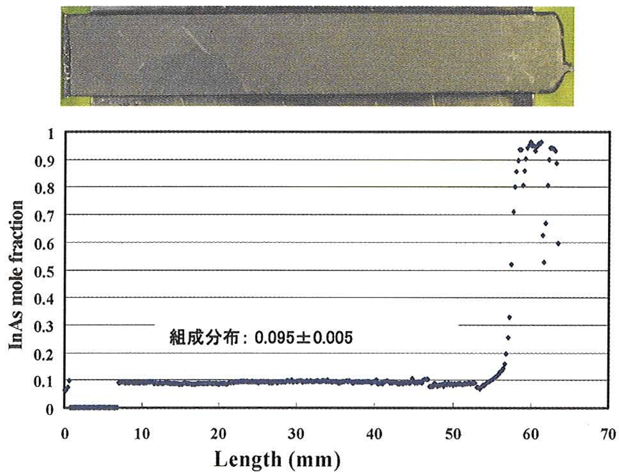


Fig. 2. InAs concentration profile along with roughly polished surface of an $In_{0.1}Ga_{0.9}As$ crystal from a GaAs seed by the TLZ method

InAs concentration ranges from 0.09 to 0.10 mole fraction with scattering of less than ±0.005 and shows excellent compositional uniformity. Such compositional uniformity is almost the same as that obtained in 2 mm capillary crystals in which the maximum convective flow in a melt is analyzed to be below 1.4 mm/h and the diffusive mass transport is dominant in the crystal growth [4]. Similarity of excellent compositional uniformity between the 2 mm diameter crystals and 2 mm thick platy crystals supports the hypothesis that the convection in a melt is sufficiently suppressed by limiting the thickness of a platy crystal to 2 mm, namely limiting the dept of a rectangular melt. Lattice mismatch between GaAs and $In_{0.1}Ga_{0.9}As$ is about 0.7%, which is a little higher than the reported tolerable lattice mismatch in the InAs-GaAs system [6]. Therefore, poly crystallization occurred at the growth interface between the GaAs seed. However, a large single grain began to grow at the position of 25 mm and the single grain extended to the full width and to a distance of longer than 30 mm in the axial direction. The orientation of the grown crystal was <110> with {100} surfaces in the radial direction. Repeated crystal growth experiments confirmed reproducibility of single crystal growth with the same orientation and similar compositional uniformity by the TLZ method. For about the total of 30 experiments, single crystals were grown in all cases. Such results may also imply the importance of suppressing convection in the melt for obtaining single crystals because no single crystals were obtained in 10 mm diameter crystals in which convective flow in a melt was analyzed to be more than 2500 times as high as the 2 mm diameter crystals.

Since we have succeeded in growing homogeneous 10 mm wide $In_{0.1}Ga_{0.9}As$ platy crystals repeatedly, we tried to grow wider platy crystals in the next step. As described in the introduction, wider platy crystals with uniform composition should be grown if convection in a rectangular melt is suppressed by its small thickness. Sample configuration, thickness of the sample (2 mm) and growth conditions were the same as 10 mm wide crystals and 20 mm wide platy crystals were grown. Roughly polished surface of a 20 mm wide $In_{0.1}Ga_{0.9}As$ crystal are shown in Fig. 3. At the initial growth interface between a GaAs seed, poly crystallization occurred but as is the case of 10 mm wide crystal, a large single crystal grain with 20 mm×25 mm grew after about 15 mm growth.

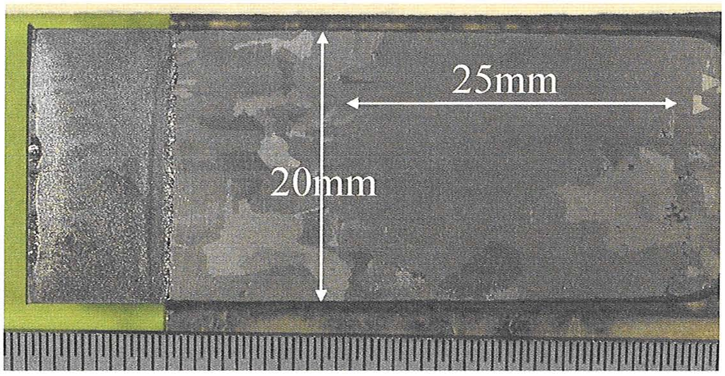


Fig. 3. 20mm wide platy crystal of $In_{0.1}Ga_{0.9}As$. Note that a large grain grew at the distance of about 15mm from the seed-crystal interface.

In, Ga, and As concentration profiles along the center line of the crystal were shown in Fig. 4. Note that uniform composition was obtained for a distance of about 35 mm. To confirm over all uniformity in the grown crystal, mapping analyses of composition was performed on the polished surface of the grown crystal. Results are shown in Fig. 5. No singular region exists in the plane and uniform composition was obtained for the area of 20 mm×35 mm. Such excellent compositional uniformity in the full range of 20 mm width verifies the validity of suppressing convection by limiting the melt thickness and the width of the melt is not an important factor. Therefore, the result shows that wider platy crystals can be grown in principle and is beneficial for cost reduction of substrates fabricated by this method.

For substrate use, crystal quality is very important. To investigate the crystal quality, X-ray rocking curves were measured on the mirror polished surfaces. FWHM of about 0.01 degree was observed for a GaAs seed. The 10 mm wide $In_{0.1}Ga_{0.9}As$ platy crystals showed FWHM of 0.02～0.05° as shown in Fig, 6 (a) and these values were acceptable for substrates of laser diodes. FWHM for 20 mm wide crystals were a little broaden to 0.04～0.06° as shown in Fig. 6(b).

The reason is not clear in the present stage but we think that deterioration of crystal quality in a wide crystal may arise from thermal condition change due to scale up than the increase in convective flow in a melt. The wider crystal growth has just started and the number of grown crystals is scarce and the most appropriate growth conditions may not be applied. Improvement of crystal quality in wider crystals will be achieved by the successive crystal growth and by finding the most suitable growth conditions.

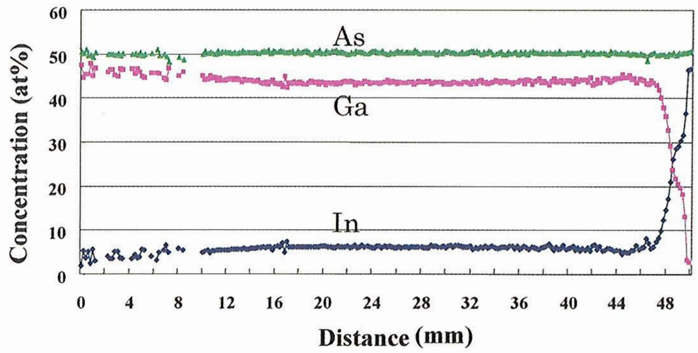


Fig. 4. Compositional profiles of a 20mm wide platy crystal along the center line in the growth direction.

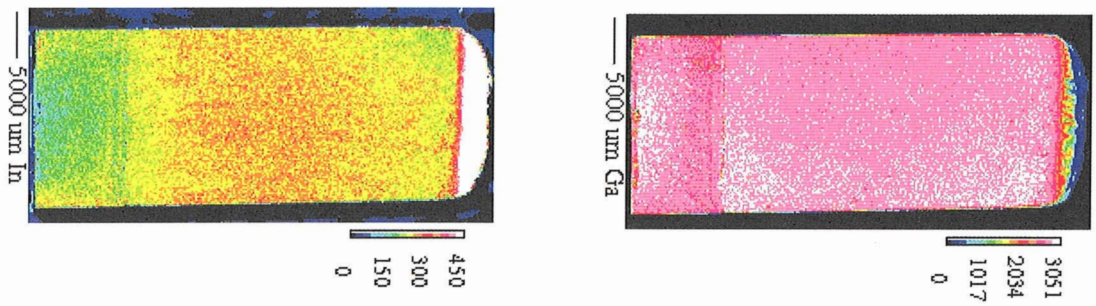
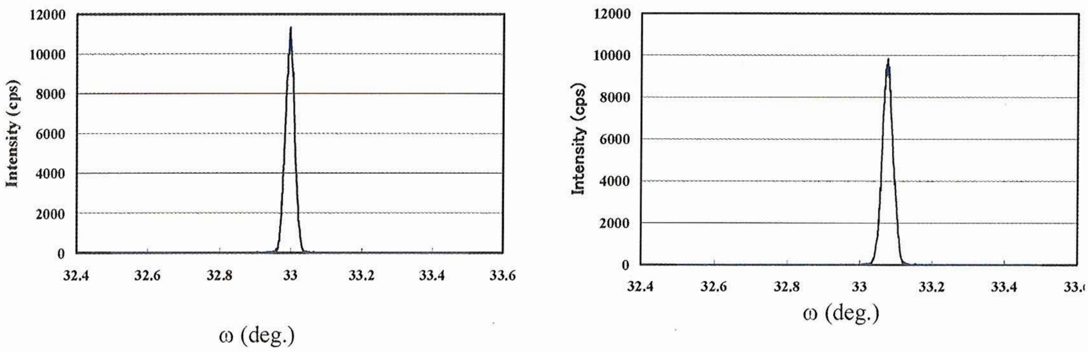


Fig. 5. Mapping analyses of In and Ga distributions in the surface of a 20mm wide platy crystal.



(a) 10mm wide platy crystal of $In_{0.1}Ga_{0.9}As$
FWHM=0.04°

(b) 20mm wide platy crystal of $In_{0.1}Ga_{0.9}As$
FWHM=0.06°

Fig. 6. X-ray rocking curve of (400) reflection in comparison of 10mm wide crystal with that of 20mm wide $In_{0.1}Ga_{0.9}As$ crystal.

5. Summary

We succeeded in growing 20mm wide platy homogeneous $In_{0.1}Ga_{0.9}As$ single crystals for substrate use by the traveling liquidus zone (TLZ) method. The thin platy shape is beneficial to suppress convection in a melt during crystal growth and to obtain compositionally uniform crystals. Platy shape is also beneficial to obtain sufficient area for substrate use. Excellent compositional uniformity of wide crystals confirmed the hypothesis that convection is suppressed when the melt thickness is limited and its width is not a dominant factor for convection. However, x-ray rocking curve of 20mm wide crystal is a little broader than that of 10mm wide crystal. We think that such deterioration of crystal quality in 20mm wide crystals arises from thermal condition mismatch during crystal growth and quality of 20mm wide crystals will be improved to the level of 10mm wide crystals when growth conditions are optimized. Anyway, successful scale up of the crystal is the first step for producing commercial use large substrates.

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