ISSN 1349-1113
JAXA-RR-07-015E

JAXA Research and Development Report

Scale up of $In_xGa_{1-x}As$ (x: 0.08 - 0.13) Platy Crystals for Semiconductor Laser Substrates

Kyoichi KINOSHITA, Toshiaki UEDA, Satoshi ADACHI,
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February 2008

Japan Aerospace Exploration Agency

Scale up of $In_xGa_{1-x}As$ (x: 0.08 - 0.13) Platy Crystals for Semiconductor Laser Substrates

By

Kyoichi KINOSHITA*, Toshiaki UEDA, Satoshi ADACHI, Yasutomo ARAI, and Shinichi YODA

Abstract: We have succeeded in growing large and high quality platy $In_xGa_{1-x}As$ (x: 0.08 - 0.13) single crystals by the traveling liquidus-zone (TLZ) method. This year we studied scale up of platy crystals for commercialization of laser diodes as well as improvement of crystal quality. A 30 mm wide $In_{0.09}Ga_{0.91}As$ single crystal having high quality area larger than $15 \times 40 mm^2$ was grown. Simultaneous two platy crystals growth was also successful. These results show scale up of platy crystals and mass production of substrates are possible in principle without the change of growth configuration.

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

1. Introduction

$In_xGa_{1-x}As$ (x: 0.1 - 0.2) single crystals are promising as substrates of laser diodes for wavelength of 1.3 µm used in the optical communication system. However, the growth of such ternary bulk single crystals with uniform composition is not easy and high quality substrates have not been prepared before we succeeded in growing $In_xGa_{1-x}As$ (x: 0.1 - 0.13) platy crystals by the TLZ method. The TLZ method, which we originally invented for homogeneous alloy crystal growth in microgravity [1-3], requires diffusion limited mass transport and convection in a melt should be avoided. In order to fulfill both requirements of large surface area for substrates and suppression of convection during crystal growth, we grew platy crystals instead of large diameter cylindrical crystals. Convection in a melt was sufficiently suppressed by limiting the thickness of platy crystals to 2 mm. As a result, homogeneous $In_xGa_{1-x}As$ (x: 0.08 - 0.13) single crystals with high quality surface area of larger than $10 \times 10 mm^2$ were grown. For substrate use, larger area is required and mass productivity is also required. This year, we studied scale up of platy crystals in preparation for commercialization of laser diodes as well as improvement of crystal quality. Here, we report on the results obtained this year.

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 relatively low temperature gradient (10 - 20℃/cm). Such zone is formed by heating material having excess InAs concentration with lower melting point adjacent to the seed. Relations among temperature distribution, 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

Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 2-1-1, Sengen, Tsukuba, Ibaraki, 305-8505 Japan
* Corresponding author, E-mail address: kinoshita.kyoichi@jaxa.jp

interface, InAs is supplied by segregation on solidification. The segregated InAs is transported toward the feed side by diffusion. At the dissolving interface of the feed side, InAs concentration increases by the transported InAs. Then the InAs concentration exceeds the equilibrium concentration at the dissolving interface and the excess InAs dissolves the feed (GaAs) in order to get into equilibrium concentration. 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 freezing 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 freezing interface shift R is calculated as

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

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 [6], R is calculated when the temperature gradient at the freezing interface $\partial T/\partial z$ is measured.

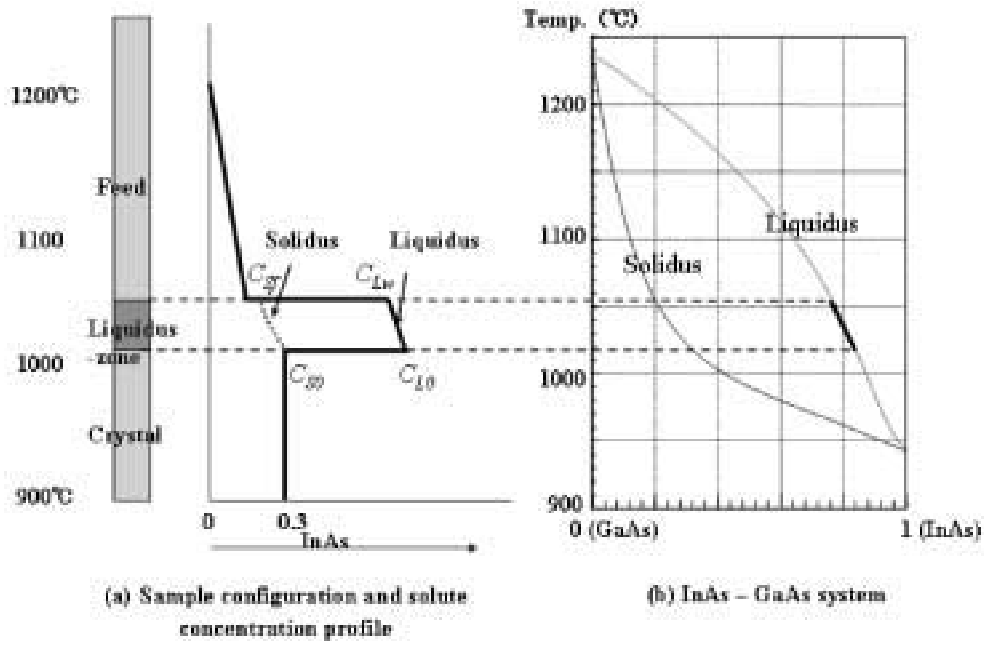


Figure 1 Principle of the TLZ method referring to the InAs-GaAs system. Relation among temperature distribution, solute concentration, liquidus-zone and the equilibrium phase diagram of the system is shown.

3. Experimental

A GaAs seed, an InAs zone former, and a GaAs feed were cut into plates with 0.65 to 2 mm thickness and 10 to 30 mm width and these were inserted into a boron nitride crucible with a rectangular bore. Orientation of seeds was <100> or <110> 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 5×10^{-5} 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 1095℃ for $In_{0.13}Ga_{0.87}As$

crystal growth. The highest temperature in the furnace was below 1192℃ so that the GaAs feed was not melted completely (cf: melting temperature of GaAs is 1238℃). The temperature gradient around 1100℃ was 22 - 28℃/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 fixed freezing interface position relative to the furnace in accordance with the freezing rate, for example 0.27 mm/h for the temperature gradient of 26℃/cm. In the 20 to 30 mm wide crystal growth, a boron nitride (BN) cap was set on a BN crucible so as to compensate temperature decrease in the BN crucible due to heat conduction increase by a large sized BN crucible. Simultaneous two crystal growth was also tried in order to check mass productivity of the TLZ method. In this case, 0.65 mm thickness samples were sandwiched with 0.65 mm thickness BN spacer and then inserted into 0.2 mm groove of the crucible. 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

4.1 Improvement of crystal quality in 20 mm wide crystals

In the 20 mm wide crystal growth, crystal growth often ended at a middle of a feed as shown in Fig. 2, although the growth conditions were same as the 10 mm wide crystal. This was interpreted that heat loss towards the lower temperature side increased in 20 mm wide crystal because the cross sectional area of a BN crucible (which has higher thermal conductivity than that of InGaAs and also than that of quartz) increased in proportional to square of the crucible radius. Heat loss in a small diameter crucible and that in a large diameter crucible is schematically compared in Fig. 3.

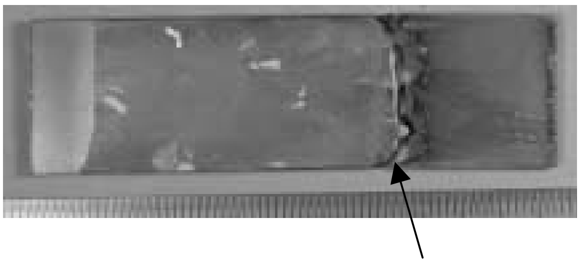


Fig. 2 A 20mm wide platy crystal. growth ended at the marked position.

As a counter measure to the heat loss, we put on a BN cap on a crucible as shown in Fig. 4. The cap located at a higher temperature region and was expected to receive radiated heat and transfer the heat to the crucible at a lower temperature region and compensate heat loss in the 20 mm crystal growth. A 20 mm wide crystal grown using this cap is shown in Fig. 5. The picture shows an as-grown crystal. Note that no separation of a grown crystal and a feed occurred. A 2×3 mm^2 grain was found in a single crystal region. In a wide crystal, suppression of grain growth from a wall of crucible is more important because surface area of a platy crystal increases in proportional to the width.

Compositional profiles of a grown crystal are also shown in Fig. 5. Note that InAs concentration is uniform from a distance of 20 mm to 44 mm. The average InAs concentration in this region is 0.09 and concentration fluctuation is less than 0.004 in mole fraction. Full width at half maximum of an X-ray rocking curve (FWHM) is about 0.03° in this compositionally uniform region and shows improved crystallinity. It is evident that the cap served as a heat capacitor as expected and heat was supplied to a BN crucible and hence to a feed in the BN crucible.

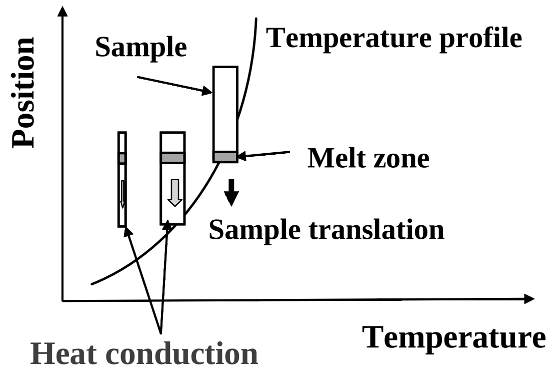


Fig. 3 Comparison of heat flow between a small and a large diameter sample (crucible). Note that heat flow from high temperature to lower temperature region increases in proportional to square of a crucible diameter.

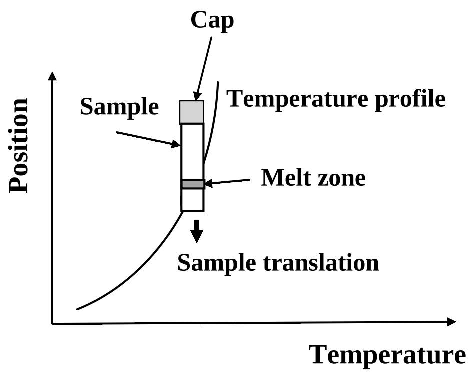


Fig. 4 Revised sample configuration for heating a sample end. A BN cap was put on a crucible.

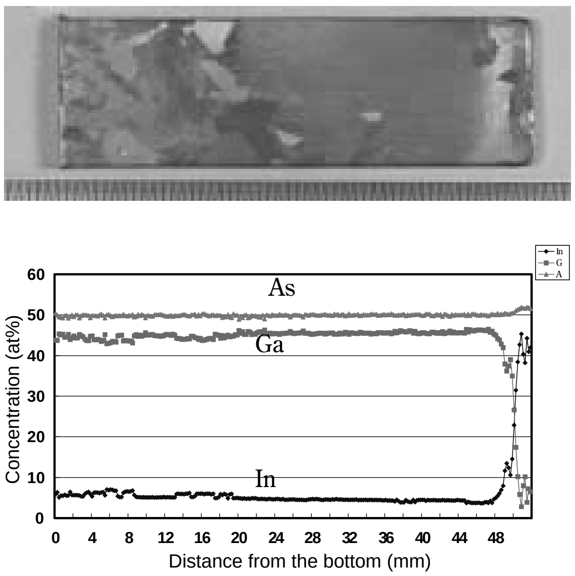


Fig. 5 As grown crystal surface (top) and compositional profiles along the center axis of the crystal measured by an EPMA.

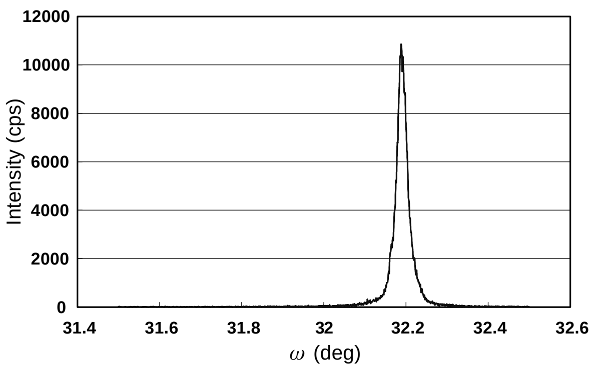
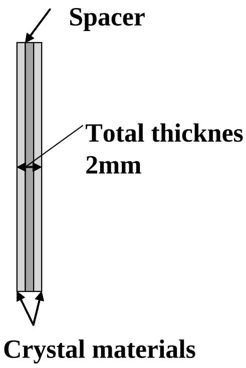


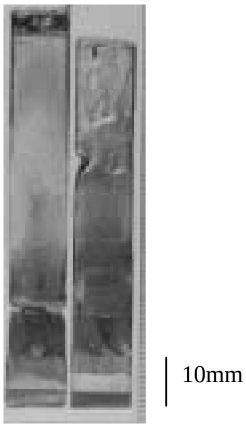
Fig. 6 X ray rocking curve of a 20 mm wide crystal.

4.2 Simultaneous two crystal growth

One way to improve productivity of crystal growth is simultaneous multi crystals growth. In order to check the feasibility of this method, simultaneous two crystals growth was tried. In this case crystal width is 10 mm and thickness is 0.65 mm. A 0.65 mm BN spacer was sandwiched between two sets of crystal materials (a feed, a zone former and a feed) and was put into 2.0 mm groove of a BN crucible. The sandwiched sample device is shown in Fig. 7 (a). The growth conditions were same to those of single 10 mm wide crystal growth. Two crystals after growth procedures are shown in Fig. 7 (b). A crystal (right side one) was normally processed, but in the other crystal (left side one) InAs zone was separated from a GaAs feed and the TLZ growth was unsuccessful. The reason is that the BN spacer inclined and hindered the drop of a feed into melt zone for the left side crystal. However, the result shows that two crystals simultaneous growth is possible if the inclination of a spacer is prevented. Since a thin crystal with 0.65 mm thickness was successfully grown, simultaneous multi crystal growth more than 2 is expected by controlling spacer position well. The compositional profiles along the center axis of the successfully grown crystal are shown in Fig. 8. This compositional profiles show that the crystal was grown by the TLZ process as described above. Uniform region was obtained from the distance of 8 mm to 32 mm. The average InAs concentration in this region is 0.13 in mole fraction ($In_{0.13}Ga_{0.87}As$) and compositional fluctuation was less than 0.005 mole fraction. An X-ray rocking curve of this crystal is shown in Fig. 9. FWHM is about 0.05° and this value is a little worse than the best 10 mm wide crystal. This is the first try and higher quality crystals will be grown when growth conditions are optimized.



(a)



(b)

Fig. 7 Growth configuration for simultaneous two crystals growth and as-grown crystals. The left side crystal was unsuccessful but the right side one was successful.

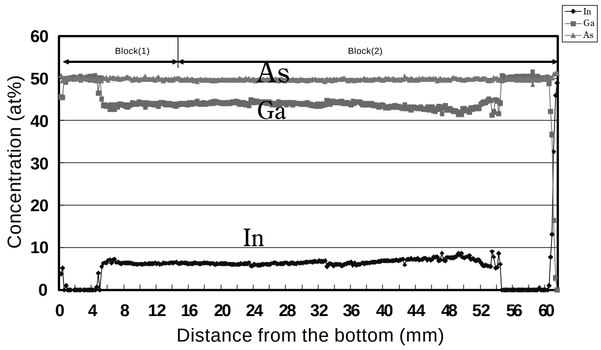


Fig. 8 Compositional profiles along the center axis of a 0.65 mm thick crystal.

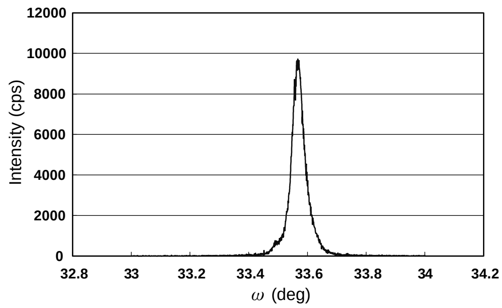


Fig. 9 An example of X-ray rocking curves for a 6.5 mm thick crystal.

4.3 30 mm wide crystal growth

Another way to improve productivity of substrate fabrication is to enlarge crystal size. In this case, the thickness is limited from the view point of convection suppression (less than 2 mm is confirmed to be effective to suppress convection in a melt during the TLZ crystal growth) as shown in Fig. 10. We therefore tried to enlarge crystal width. If convection in a melt is suppressed due to thin melt thickness, enlargement of the crystal width will not deteriorate crystal quality such as compositional uniformity and crystallinity. A 30 mm wide crystal growth was tried. A cap was used as a heat capacitor similarly to the case of 20 mm wide crystal growth. In the growth, lateral growth was also tried. The TLZ method requires slow growth rate for obtaining homogeneous crystals for example 0.22 mm/h at a temperature gradient of 10℃/cm and hence needs much time for crystal growth. If lateral growth is possible, crystal growth is much productive because simultaneously many crystals can be grown. For this purpose, growth configuration was a little changed. The growth configuration is shown in Fig. 11. Two seeds were used; one was set at the bottom of a crucible and the other was set at the right side of the crucible. The growth conditions were almost same as those of the 20 mm wide crystal growth. A little change is a freezing interface temperature. It was 1097.7℃ although it was about 1080℃ for 20 mm wide crystal growth.

Roughly polished surface of a grown crystal is shown in Fig. 12. Three large grains were observed; 15×40mm^2, 8×12mm^2, and 6×12mm^2. Two grains (15×40mm^2 and 6×12mm^2) have {100} surfaces and can be used as substrates for 1.3μm wavelength laser diodes. Result of Ga concentration mapping analysis as well as growth directions (arrows) is shown in Fig. 13. Uniform concentration region extends from the left bottom to the right top. Two seeds became slim but remained unmelted. When we note the bottom region, seed was grown to be ternary crystals having the composition of $In_{0.09}Ga_{0.91}As$ in the left corner. Lateral growth (growth to the radial direction) might occur as shown by an arrow in Fig. 13. Lateral growth can also be observed in the upper region as shown by arrows as the seed became slim.

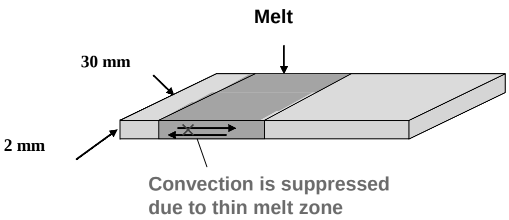


Fig. 10 Suppression of convection due to thin melt zone.

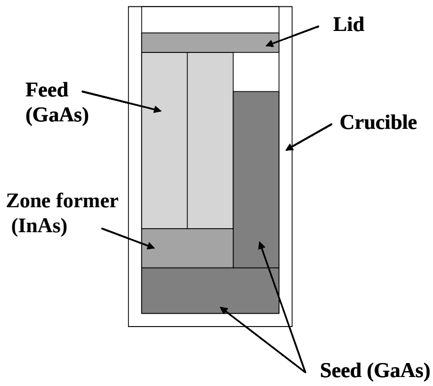


Fig. 11 Growth configuration of a 30 mm wide platy crystal.

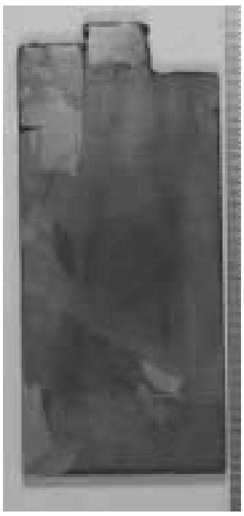


Fig. 12 Roughly polished surface of a 30 mm wide crystal.

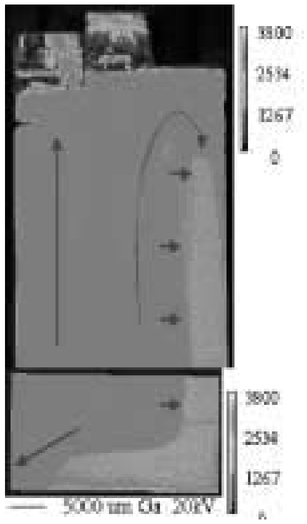


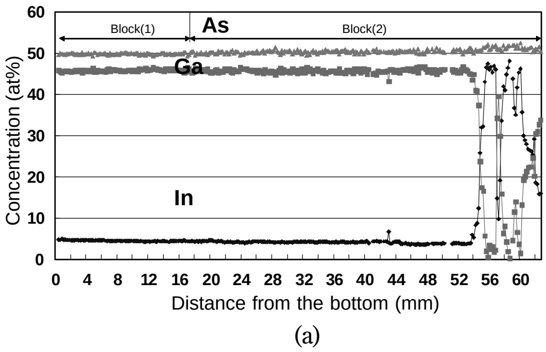
Fig. 13 Ga concentration mapping and growth directions (arrows) for the 30 mm wide crystal.

Compositional profiles along the left peripheral (1mm inside from the peripheral) and along the center line are shown in Figs. 14 (a) and (b). As described above, in the left region composition of $In_{0.09}Ga_{0.91}As$ extends to a distance longer than 50 mm from the beginning of crystal growth. In the central region, compositionally uniform region also extends to about 50 mm length.

X ray rocking curves were measured along the center axis. Results are shown in Fig. 15. Values of full width at half maximum (FWHM) of each rocking curve are listed in table 1. FWHM values were deteriorated at around 30 and 35 mm position. When we look at Fig. 14 (b), compositional fluctuation increased in this region. Compositional fluctuation in this region is $\pm$0.01 in InAs mole fraction while it is $\pm$0.005 in the low FWHM value region. When compositional fluctuation occurs, lattice change occurs and lattice mismatch among the nearby lattices is induced. Lattice mismatch causes mechanical stress to nearby lattices and peaks of X-ray rocking curves will be broaden. Therefore, control of compositional uniformity is strongly required in alloy crystal growth. As reported previously [7], temperature stability is the most dominant factor for achieving compositional uniformity. From this view point, scale-up of grown crystal is favored because temperature fluctuation decreases due to increase of heat capacity of a sample.

4.4 Laser diode fabrication using platy crystals as substrates

Our co-investigators (NTT Photonics Laboratory) fabricated laser diodes using our crystals as substrates. The lasing wavelength at 25℃ is 1.31 μm (Fig. 16). Threshold currents were about 20 mA at 25℃ and about 45 mA at 95℃, respectively. Output power higher than 10 mW was obtained at 95℃. These data show good lasing characteristics of the fabricated laser [7]. Such high temperature stability was first realized and show superiority of our ternary crystals.



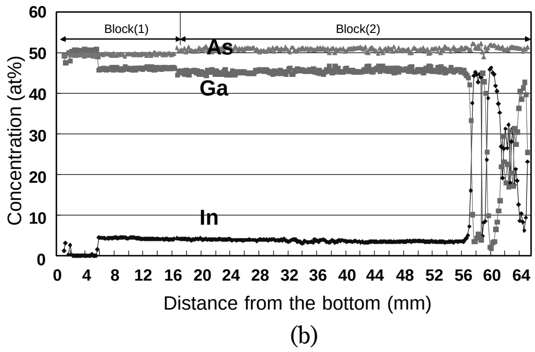


Fig. 14 Compositional profiles of a 30mm wide crystal (a): along the left peripheral (1mm inside), (b): along a center axis..

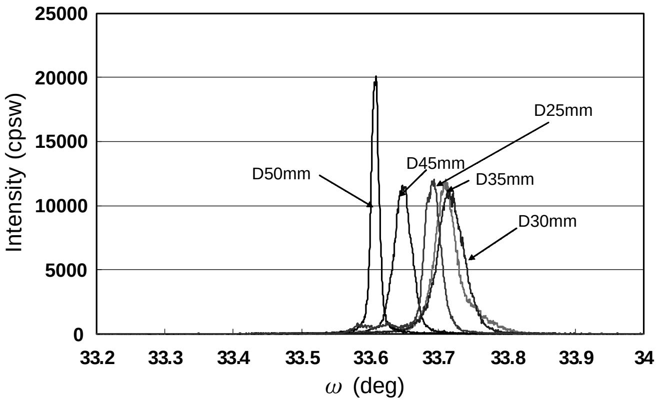


Fig. 15 X-ray rocking curves at different 5 positions. Positions correspond to a distance in Fig.14

Table 1. FWHM values at 5 positions.

Position	FWHM (deg)
D25	0.028
D30	0.044
D35	0.037
D45	0.031
D50	0.014

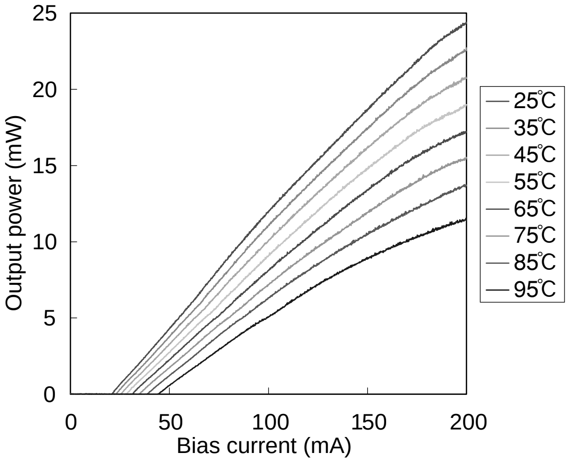


Fig. 16 (a) **Temperature dependence of I-L characteristics under pulsed operation.**

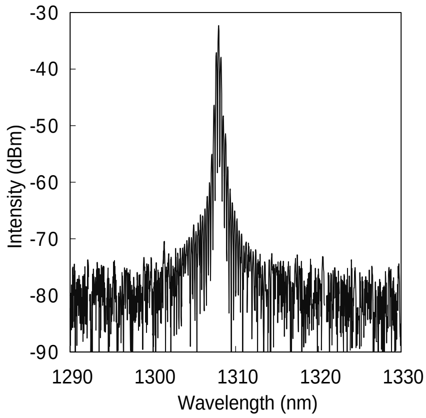


Fig. 16 (b) **Lasing spectrum of fabricated broad-ridge laser under CW operation.**

5. Summary

We have investigated scale up of platy crystal growth by the TLZ method for mass production of substrates used in laser diode fabrication. Simultaneous two plate crystals growth and enlargement of crystal width were studied. In the simultaneous two crystals growth, we succeeded in growing a crystal of 10×50 mm^2 area and 0.65mm thickness. A 30 mm wide $In_{0.09}Ga_{0.91}As$ single crystal having high quality area larger than 15×40mm^2 was also grown. These results show possibility of scale up of platy crystals and mass production of substrates without the change of growth configuration. A 30 mm wide crystal also showed possibility of lateral growth by the TLZ method. The lateral growth will further beneficial for mass production of substrates.

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JAXA Research and Development Report JAXA-RR-07-015E

Date of Issue : February 29, 2008
Edited and Published by : Japan Aerospace Exploration Agency
7-44-1 Jindaiji-higashimachi, Chofu-shi, Tokyo 182-8522, Japan
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