ISSN 1349-1113
JAXA-RR-06-014E

JAXA Research and Development Report

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March 2007

Japan Aerospace Exploration Agency

High Quality $In_xGa_{1-x}As$ (x: 0.1–0.13) Platy Crystal Growth for Semiconductor Laser Substrates

By

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Abstract: We have succeeded in growing large and high quality platy $In_xGa_{1-x}As$ (x: 0.1–0.13) single crystals by the traveling liquidus–zone (TLZ) method. Among factors which affect crystal quality, the most influential factor is temperature stability at the growth region when the composition of grown crystals is in the range between $In_{0.1}Ga_{0.9}As$ and $In_{0.13}Ga_{0.87}As$; when the temperature stability was better than ±0.1℃, compositional uniformity was 0.13 with σ of 0.001 where σ is the standard deviation, and 0.13 with σ of 0.006 when the temperature stability was ±0.2℃. The appropriate temperatures at the feed region were between 1170 and 1180℃. Temperature gradient also affected crystal quality through the variation of growth rate. Temperature gradients chosen for high quality crystal growth were in the range between 25 and 28℃/cm, which were measured outside of quartz ampoules. Finally, $In_{0.13}Ga_{0.87}As$ single crystals having high quality area larger than 10×30mm^2 were reproducibly grown. Such large and high quality bulk single crystals which can be used as substrates of laser diodes operating at the wavelength of 1.3 μm were grown for the first time.

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: 0.1–0.2) 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: 0.1–0.2) single crystals with high quality surface area of larger than 10×10mm^2 were grown. For substrate use, larger area is required and mass productivity is also required. This year, we studied factors affecting crystal quality in detail and succeeded in growing crystals with high quality surface area larger than 10×30mm^2. Here, we report on the results obtained this year.

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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 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 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 freezing interface shift R is calculated as

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

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

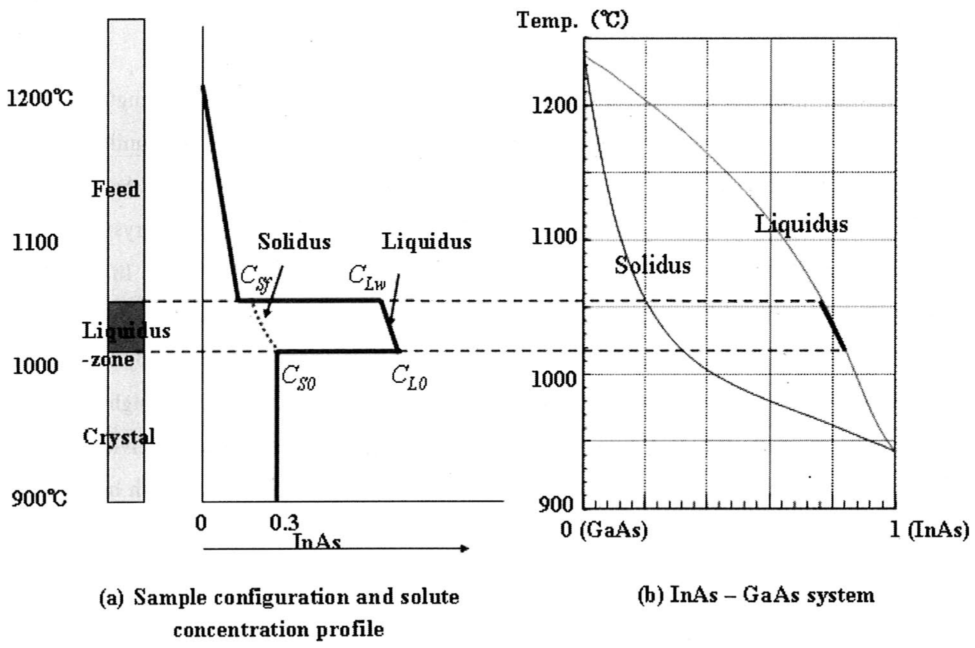


Figure 1 Principle of the TLZ method referring to the InAs–GaAs system. Relation among temperature distribution, solute concentration, liquidus–zone and the equilibrium phase diagram of the system is shown.

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 at the sample translation rate which is calculated by the eq. (1) but the direction of translation is opposite to the freezing interface shift. 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 in order to maintain controlled concentration gradient in a melt zone.

3. Experimental

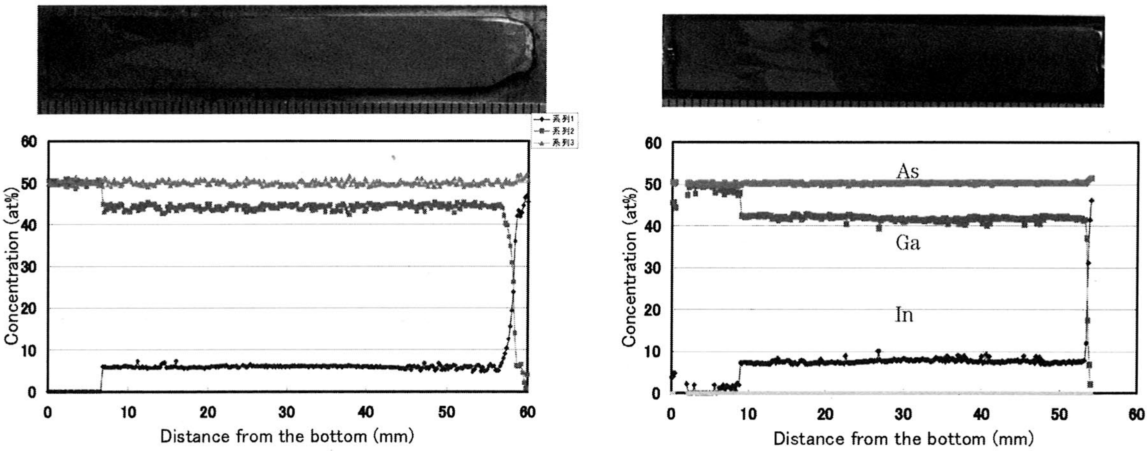
A GaAs seed, an InAs zone former, and a GaAs feed were cut into plates with 2 mm thickness and 10 or 20 mm width and these were inserted into a boron nitride crucible with a rectangular bore. The orientation of the seed was <100> with {100} surfaces perpendicular to the growth axis and the length of the feed was 40 or 50 mm. The crucible was then sealed in vacuum in a quartz ampoule at about 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 1190℃ so that the GaAs feed was not melted completely. The temperature gradient around 1100℃ was 22–38℃/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 of 0.27 mm/h as calculated by the equation (1) when the temperature gradient was 26℃/cm. Factors affecting crystal quality are growth temperature, temperature stability, temperature gradient in a melt, temperatures in the feed region and TLZ growth experiments were performed by varying one of these factors with setting the rest of the factors fixed in order to evaluate the effect of these factors one by one. 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 Effect of growth temperature

First, effect of growth temperature on compositional uniformity was investigated. In the alloy crystal growth, composition of the grown crystal is determined by the growth temperature (temperature at the freezing interface) where the solute is saturated. If the freezing temperature is higher, crystals with lower In concentration will be grown as is understood by the phase diagram as shown in Fig. 1. One of merits of the TLZ method is controllability of the freezing interface temperature because translation rate of the freezing interface is calculated by eq. (1) and is predicted; its position is fixed when the sample is translated so as to compensate the interface shift based on the calculation. Figure 2 compares compositional profiles along the center axis for two platy crystals with different average composition (a) $In_{0.13}Ga_{0.87}As$ and (b) $In_{0.15}Ga_{0.85}As$. In the figure, roughly polished surface photograph is also shown for referring to the single crystal region. In the $In_{0.15}Ga_{0.85}As$ crystal, InAs concentration was measured as 0.15 with σ of 0.005 where σ is the standard deviation in the distance between 30 and 40mm while it is 0.13 with σ of 0.001 in the $In_{0.13}Ga_{0.87}As$ crystal in the distance between 30 and 40mm. The reason why the compositional fluctuation of $In_{0.13}Ga_{0.87}As$ is less than the crystal with higher In concentration ($In_{0.15}Ga_{0.85}As$) may originate from the fact that the separation of liquidus and solidus is smaller as the composition approaches to the end member (GaAs or InAs). The most appropriate composition should be determined from two points of view, that is, from the view point of crystal quality and from the view point of a lattice parameter for substrate use. According to our results, if active layers for 1.3μm wavelength laser emission is grown on the $In_{0.13}Ga_{0.87}As$ substrate, mass production of laser diodes on InGaAs substrates will come true although it is usually said that substrates with the composition between $In_{0.2}Ga_{0.8}As$ and $In_{0.3}Ga_{0.7}As$ are required for 1.3

μm wavelength laser emission.



(a) (b)

Figure 2 InAs concentration profile along with roughly polished surface of an $In_{0.13}Ga_{0.87}As$ crystal (a) and an $In_{0.15}Ga_{0.87}As$ crystal (b).

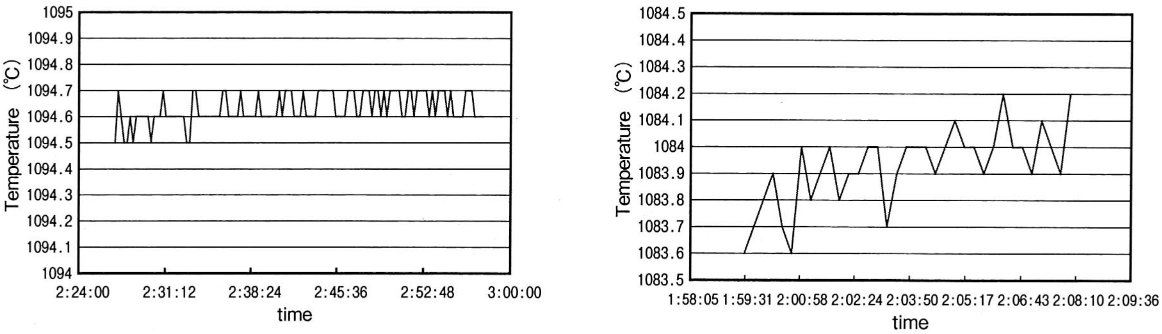
4.2 Effect of temperature stability

Effect of temperature stability on compositional uniformity was investigated on crystals with average composition of $In_{0.13}Ga_{0.87}As$. The most stable temperature was obtained when air flow in a furnace was shut. Temperature stability was ±0.1 ℃ as shown in Fig. 3 (a). With air flow conditions, temperature stability got worse to ±0.2℃ as shown in Fig. 3 (b). The stability difference was small but this small difference gave a considerable effect on the compositional uniformity as shown in Fig. 4. When the temperature stability was ±0.1℃, InAs concentration uniformity was 0.13 with σ of 0.0005 where σ is the standard deviation in the distance between 20 and 40mm. When the temperature stability was ±0.2℃, InAs concentration uniformity was 0.13 with σ of 0.006 in the distance between 20 and 40mm. The reason why the temperature fluctuation influence on the compositional uniformity may be related to the crystallization from the almost saturated melt, namely, temperature fluctuation gives rise to the formation of constitutional supercooling region in a melt and such region crystallize earlier, then it is not strange that earlier crystallized region has lower In concentration.

Improvement in compositional stability resulted in improvement of crystal quality. Figure 5 shows X–ray rocking curves in the distance between 26 mm and 56 mm at an interval of 5mm for the crystal grown at the temperature stability of ±0.1℃. Full width at half maximum (FWHM) of rocking curve ranges from 0.03 to 0.04 degrees. Such small FWHM shows good crystallineity which can be used as a substrate of laser diodes. Before improvement of temperature stability, high quality region was limited to 10×10mm^2 but high quality region extended to 10×30mm^2 after improvement in temperature stability as is shown in Fig. 5.

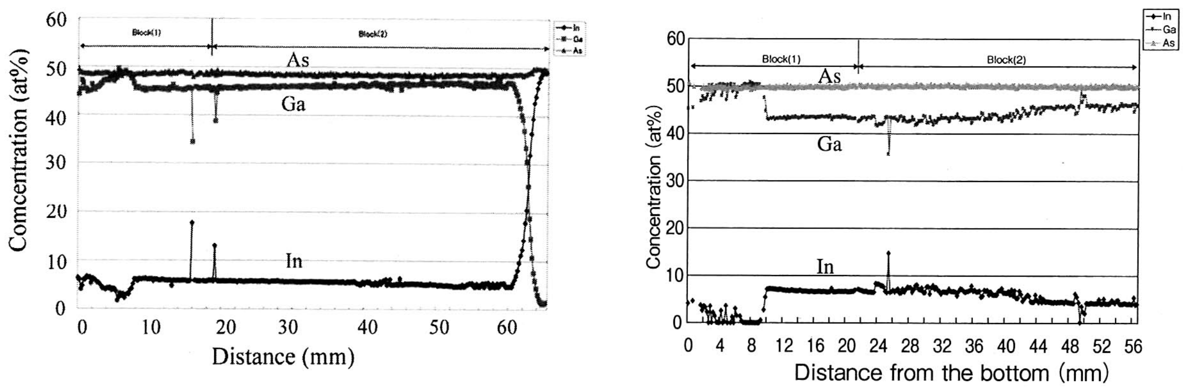
4.3 Effect of temperature gradient

In the TLZ method, temperature gradient is an important factor which controls concentration gradient in a melt and hence controls the translation rate of the freezing interface. For obtaining compositional uniformity in the growth direction, the sample device is translated in accordance with the freezing rate, which is calculated using eq. (1). Therefore, the coincidence between the temperature gradient determined freezing rate and sample translation rate is important for achieving axial compositional uniformity. In principle, compositional uniformity is obtained irrespective of the temperature gradient as long as the sample translation rate matched with the freezing rate as described above. However, the TLZ method consists of two processes, that is, melting of a solid feed and crystallization of the melt and hence there arises possibility that the rate of crystallization influence on compositional stability even if the sample translation rate matches with the freezing rate. The relation between high and low temperature gradients and compositional fluctuation was investigated in this study. Figure 6 compares two crystals grown at different temperature gradient (a): 27℃/cm and (b) 36℃/cm. Note that the crystal grown at the temperature gradient of 36℃/cm is not uniform: Indium concentration increases gradually from 6 to 10at% in the distance of 8 to 20mm. This shows that the sample translation rate did not match with the freezing rate. After In concentration reached 10 at%, uniform concentration was realized. This means that the sample translation rate matched with the freezing rate in this region. The reason why the sample translation rate matched in this region may be due to freezing rate change because the sample was translated at a constant rate; when the freezing interface shifted to lower temperature region, temperature gradient changed to the higher one and it caused to increase the freezing rate, resulting in matching of the freezing rate with the sample translation rate. Compositional uniformity of the crystal grown at the temperature gradient of 27℃/cm is rather good from the beginning of the crystal growth (9mm position). In concentration fluctuation was about ±1at% in the crystal grown



(a) (b)

Fig. 3 Comparison of temperature stability (a): ± 0.1℃ and (b): ± 0.2℃



(a) (b)

Fig. 4 Comparison of concentration profiles for two crystals with average composition of $In_{0.13}Ga_{0.87}As$ grown at different temperature stability (a): ± 0.1℃ and (b): ± 0.2℃.

at 27℃/cm, while it was about ±2at% in the crystal grown at 36℃/cm. The crystal grown at lower temperature gradient took longer time than those grown at higher temperature gradients since the growth rate is proportional to the temperature gradient as is given by eq. (1). Then, it can be implied that the interdiffusion between InAs and GaAs is more sufficient in the crystal grown at low growth rate and compositional uniformity is improved. When the temperature gradient is higher, freezing interface shape becomes more concave due to thermal conductivity difference between the crucible and growing crystal and the concave region crystallizes later than the convex region resulting in increase of compositional fluctuation.

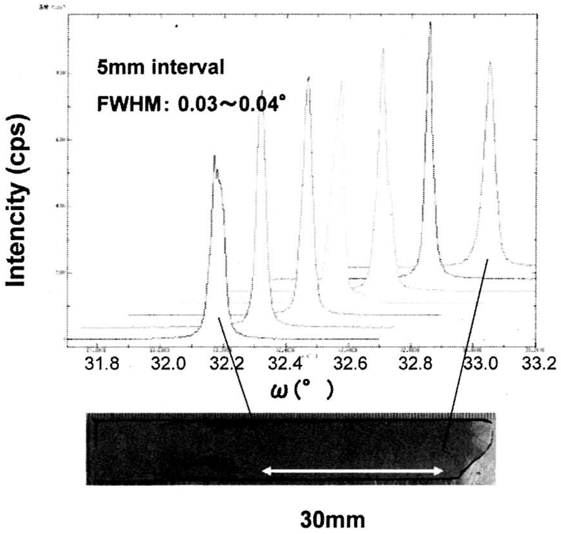


Fig. 5 Full width at half maximum (FWHM) plots at 5mm intervals from 26 to 56mm of the TLZ–grown crystal at the temperature stability of ±0.1℃.

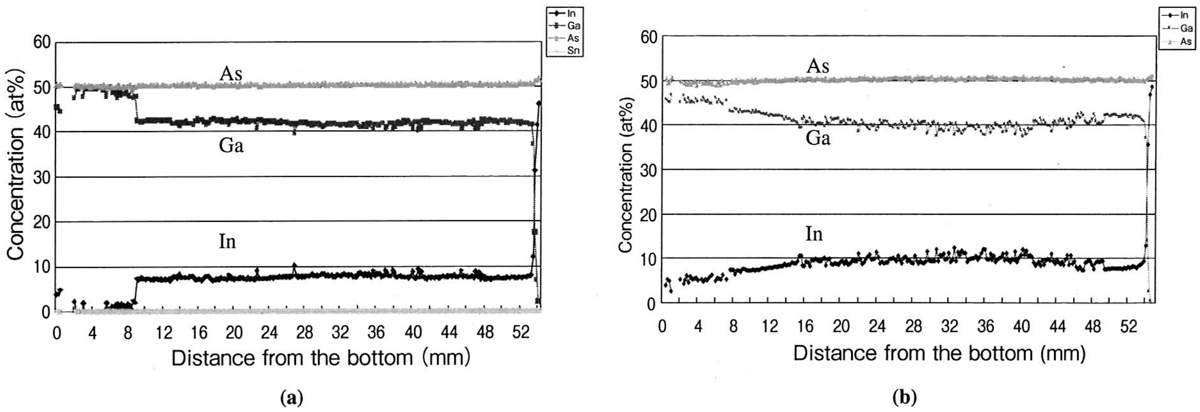


Fig. 6 Comparison of compositional profiles of crystals grown at different temperature gradients, (a): 27℃/cm, (b): 36℃/cm.

4.4 Effect of temperatures in the feed

Temperature in the feed region also affected crystal quality, especially growth length was limited when the feed temperatures were below 1150℃, while we usually grow crystals at feed region temperature between 1170 and 1180℃. Figure 7 shows ending of the crystal growth by the separation of a grown crystal and a feed. The mechanism is not well understood but such separation repeatedly occurred when the feed region temperatures were around 1150℃. It may be considered that a melt zone between the top of a growing crystal and a feed loses its ability to dissolve a feed sufficiently due to increase in viscosity when the feed temperature is low. Then, the feed cannot travel towards the higher temperature region. In such conditions, the TLZ growth mechanism does not work well and instead, the melt is directionally solidified; when the sample is translated towards lower temperature side, In accumulates in the region adjacent to the feed due to segregation. In this case, the accumulated In forms the inverse concentration gradient compared with the TLZ method. It may be possible that the separation of the feed to the grown crystal occurs when the accumulated In melts again the feed .

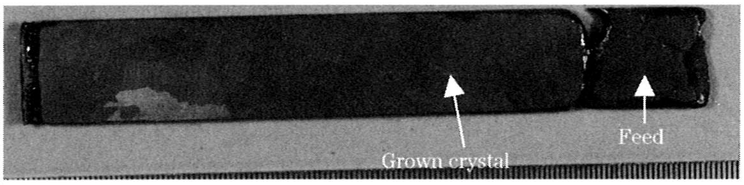


Fig. 7 Roughly polished surface of a crystal grown at the feed temperatures of about 1145℃. The grown crystal (left) was separated to the feed (right) at about 50mm position

5. Summary

We investigated factors which affect quality of TLZ–grown platy crystals. They are freezing interface temperature, temperature stability, temperature gradient and feed region temperature. The freezing interface temperature controls the composition of the grown crystal in alloy crystal growth and it affected compositional uniformity to large extent. The higher temperature (the lower In concentration) gave higher crystal quality. In the study of the effect of temperature stability, temperature gradient and feed region temperature on crystal quality, the composition was fixed to around $In_{0.13}Ga_{0.87}As$. When the temperature stability was set at ±0.1℃, compositional uniformity improved compared to the temperature stability ±0.2℃; the standard deviation of InAs concentration was reduced from 0.006 to 0.001 mole fraction. The appropriate temperatures at the feed region were between 1170 and 1180℃. Temperature gradient also affected crystal quality through the variation of growth rate. Finally, $In_{0.13}Ga_{0.87}As$ single crystals having high quality area larger than $10\times30mm^2$ were reproducibly grown. Such large and high quality InGaAs bulk single crystals were first obtained by the TLZ method and the results showed validity of the TLZ method.

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JAXA Research and Development Report JAXA-RR-06-014E

Date of Issue : March 30, 2007
Edited and Published by : Japan Aerospace Exploration Agency
7-44-1 Jindaiji-higashimachi, Chofu-shi, Tokyo 182-8522, Japan
URL : http://www.jaxa.jp/
Printed by : FUJIWARA PRINTING Co., Ltd.

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