Constitutional supercooling in the crystal growth of $In_xGa_{1-x}As$

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Abstract

The critical freezing rate for avoiding the constitutional supercooling in the crystal growth of $In_xGa_{1-x}As$ from its melt has been investigated quantitatively and it is found that the critical freezing rate is between 0.25 and 0.28 mm/h at a temperature gradient in the melt of 10℃/cm when the convection is suppressed. Since the critical freezing rate that is calculated by the criteria reported by Tiller *et al.* in the diffusion limited growth is 0.22 mm/h at 10℃/cm, it can be said that tolerance for the constitutional supercooling exists. When convection in the melt existed, the critical freezing rate for avoiding the constitutional supercooling was reduced below the Tiller's criteria. Local inhomogeneity in the melt caused by convection might increase the local constitutional supercooling even at lower growth rate. The quantitative study on the effect of convection for the constitutional supercooling in a semiconductor crystal growth is the first time.

1. Introduction

Investigation on the constitutional supercooling during the directional solidification of a melt has extensively been performed for metallic alloys [1 – 5] and Tiller *et al.* analyzed conditions for avoiding constitutional supercooling in the diffusion limited growth [6]. However, very little is known on the constitutional supercooling of semiconductor alloys due to their high vapor pressures or their high melting temperatures in such alloys. We reported that periodic concentration fluctuation observed in directionally solidified $In_xGa_{1-x}As$ crystals when the solidification rates were too fast and this phenomenon seemed to originate from the constitutional supercooling [7, 8]. But no quantitative study has ever been made since solidification rate varies in the normal freezing of an $In_{0.3}Ga_{0.7}As$ melt and accurate critical growth rate for avoiding the constitutional supercooling cannot be determined exactly.

Recently we invented a new crystal growth method named the traveling liquidus-zone method (abbreviated as the TLZ method) for growing compositionally homogeneous alloy crystals and $In_{0.3}Ga_{0.7}As$ single crystals with uniform composition (InAs concentration fluctuation of less than 0.01 mole fraction) and the uniform region length of longer than 20 mm have been grown by the TLZ method [9 - 11]. Experimental results as well as theoretical analysis show that the spontaneous freezing rate in the TLZ method is constant and a homogeneous crystal is grown when the sample device is translated in the opposite direction to the direction of spontaneous freezing in accordance with the freezing rate [9 – 11]. The relation is expressed as follows,

$$R = -V = \frac{D}{C_{L0} - C_{S0}} \left(\frac{\partial C}{\partial T} \right) \left(\frac{\partial T}{\partial z} \right)_{z=0} \quad (1),$$

where R is the translation rate of the sample device, V is the spontaneous freezing rate, D is interdiffusion coefficient between solute and solvent, C_{L0} and C_{S0} are solute concentrations in a liquid and that in a solid at the freezing interface, respectively, $\partial C/\partial T$ is reciprocal of the slope of the liquidus, $\partial T/\partial z$ is the temperature gradient in the zone, and z is the distance measured from the freezing interface.

For such growth of the constant rate, the direct and quantitative comparison with the critical condition for suppressing the constitutional supercooling is possible. More over, it is noted that the condition for growing homogeneous crystals in the TLZ method expressed as eq. (1) is rewritten as eq. (2) if notation in eq. (1) is changed as $C_{L0} = C_0/k_0$, $C_{S0} = C_0$, and $\partial C/\partial T = 1/m$.

$$\frac{G}{R} = \frac{mC_0}{D} \cdot \frac{1-k_0}{k_0} \quad (2)$$

This means that homogeneous crystals in the TLZ method are grown at just the critical growth rate for avoiding the constitutional supercooling deduced by Tiller *et al.* [6]. Therefore, the TLZ method is very interesting not only from the viewpoint of obtaining homogeneous crystals but also from the viewpoint of investigating constitutional supercooling conditions.

We examined the critical sample translation rate for avoiding the constitutional supercooling experimentally and compared it with the theoretically obtained critical growth rate by using the eq. (2) and we found that the experimentally determined critical sample translation rate was more than 14% higher than the theoretical one. The difference may be defined as tolerance for the constitutional supercooling. Then, the tolerable limit of the constitutional supercooling for the stable growth is of much interest and should be quantitatively determined. It can be said that homogeneous single crystal growth by the TLZ method is possible without constitutional supercooling owing to this tolerance. We also investigated the effect of convection on the critical conditions of the constitutional supercooling and made it clear that convection in a melt reduces the critical growth rate by causing local compositional inhomogeneity in the melt and makes single crystal growth difficult in larger diameter crystals because convection increases as the melt size increases. In this paper, we report results of the quantitative study on the constitutional supercooling during the growth of $In_{0.3}Ga_{0.7}As$ studied by using the TLZ method.

2. Experimental

Crystals were grown by the TLZ method. Since the details of the method is reported elsewhere [9], it is very briefly described below. A part of a directionally solidified ingot with InAs mole fraction of about 0.05 and about 10 mm in length was cut off and used as a seed. Combination of a directionally solidified $In_xGa_{1-x}As$ ingot with x ~ 0.1 and InAs ingot was prepared for a feed. Both the seed and the feed were cylindrically shaped and their diameter was controlled to 1.9 mm or 9.9 mm depending on the crystal size to be grown. Setting temperatures for a four zone furnace were fixed for all experiments. Temperature gradient in the liquidus-zone was measured by measuring solidus compositions at the dissolving interface as well as at the freezing interface as reported by the previous paper [11]. The temperature gradient was measured to be (10 ± 1)℃/cm. Since the spontaneous freezing rate is calculated to be 0.22 mm/h by using eq. (1) and D = 1.5 x 10^{-8} m^2/s at 1050°C [12], C_{L0} = 0.83, C_{S0} = 0.30 and $\partial C/\partial T = -1/461$ mol/°C [13], sample translation rates were set at 0.22 mm/h (synchronized growth rate for homogeneous growth and also the critical growth rate for avoiding the constitutional supercooling), 0.27 mm/h (23% higher than the critical growth rate) and 0.32 mm/h (45% higher than the critical growth rate). Stable or unstable growth was judged by observing In, Ga and As concentration distributions of grown crystals. Concentration distributions were measured by the EPMA on the polished surfaces of grown crystals. For elucidating the effect of convection, crystal diameter was varied. Numerical analysis showed that the diffusion limited growth is possible in the case of 2 mm diameter crystals, while effect of convection in the liquidus-zone is considerable in the case of 10 mm diameter crystals. Since the initial liquidus-zone width also influences the magnitude of convection, it was controlled to be 15 or 40 mm by controlling the length of InAs in the feed.

3. Results and Discussion

Figure 1 shows compositional profiles of a crystal grown at a sample translation rate of 0.22 mm/h and quenched after the growth of 24.0 mm in length. The crystal diameter was 2 mm and convection in the melt was suppressed in such a capillary tube. The rate 0.22 mm/h is the expected freezing rate obtained by our model analysis as described in eq. (1). A seed, a TLZ-grown part, a quenched liquidus-zone and a feed remained without melting are denoted in the figure.

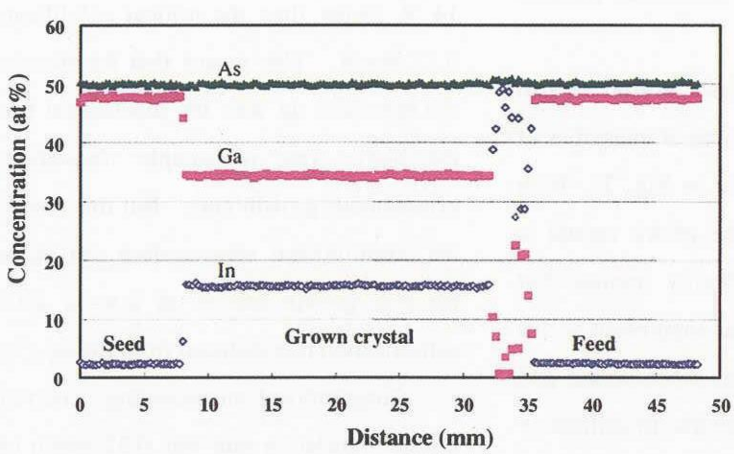

Fig. 1. Compositional profiles of a TLZ grown crystal at a sample translation rate of 0.22 mm/h. Crystal diameter is 2 mm.

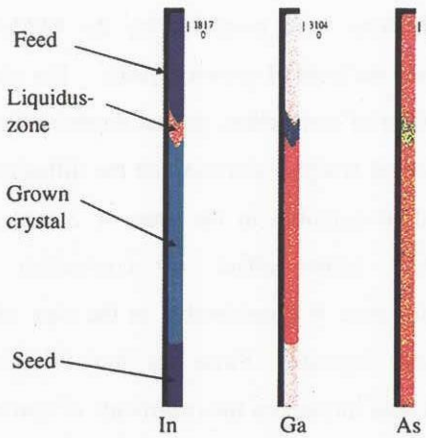

Fig. 2. EPMA mapping of In, Ga and As distributions for a TLZ grown crystal at a sample translation rate of 0.22 mm/h.

It should be noted that uniformity of the TLZ-grown part is excellent and homogeneity was established from just the beginning of the crystal growth and the homogeneous region extended to the end of the growth i.e., InAs mole fraction was controlled to be 0.30 plus or minus 0.01 in the 24 mm long TLZ-grown crystal. Uniformity of the grown crystal shows that the crystal grew synchronously to the sample translation at the rate of 0.22 mm/h. In reality, the grown crystal length 24.0 mm coincided well with the mechanical sample translation distance 24.4 mm

Homogeneity of the TLZ-grown crystal is also verified by two-dimensional mapping of intensities of the characteristic X-ray as shown in Fig. 2. Both axial and radial uniformity of the grown crystal is excellent. Such excellent uniformity implies that the constitutional supercooling was suppressed at this growth rate. If the constitutional supercooling had occurred, concentration fluctuation due to cellular or dendritic growth should have been observed [1 – 5]. Single crystallinity of the grown crystal was checked by observing number of grains in the grown crystal as described later, which also indicates suppression of constitutional supercooling during the growth.

. If the growth rate exceeds the critical growth rate, constitutional supercooling should occur. Therefore, we increased the sample translation rate. The crystal diameter was 2 mm in this case, too. Figure 3 shows concentration profiles grown at a sample translation rate of 0.27 mm/h (23% higher than the critical growth rate). Although InAs concentration increases according as crystal growth proceeded, no fluctuation of concentration was observed. Therefore, constitutional supercooling was still suppressed even at this sample translation rate. Cross sectional view of the grown crystal also showed single crystallinity and no indication of the constitutional supercooling was detected. To make sure the growth rate, the solidified length was compared with the mechanically translated length of the sample device, because growth rate does not exactly coincide with the mechanical sample translation rate in general. The solidified length was measured to be 23.8 mm as shown in Fig. 3, while the mechanically translated length was 25.6 mm. The real growth length was 1.8 mm shorter than the mechanically translated distance and the real growth rate was calculated to be 0.25 mm/h, which is about 14 % higher than the critical solidification rate of 0.22 mm/h. This means that the freezing interface did not catch up with the mechanical translation by the higher rate of sample translation than the synchronous growth rate. But this result shows that the constitutional supercooling can be prevented if the real growth rate is as low as 1.14 x critical solidification rate deduced from the eq. (2).

Constitutional supercooling occurred when the sample translation rate was 0.32 mm/h (45% higher than the critical growth rate) for a crystal with 2 mm diameter. Axial concentration profiles of the TLZ-grown crystal are shown in Fig. 4.

Concentration fluctuation was detected in this case. Such concentration fluctuation should be caused by the constitutional supercooling [8]. The mechanism is considered similarly to the well known cellular growth mechanism. When the constitutional supercooling occurs, it causes interfacial instability and a bulged part is solidified faster than the concave part. Since solidification accompanies rejection of the solute, the segregated solute accumulates in the concave part, namely, the solute concentration is low in the early solidified part, while it is high in the late solidified part. Thus, concentration fluctuation is resulted in the grown crystal when constitutional supercooling occurs. The reason why cellular growth did not occur in $In_xGa_{1-x}As$ crystal growth is interpreted by the growth rate difference between $In_xGa_{1-x}As$ and metallic alloys; the growth rate is the order of sub-mm/h for $In_xGa_{1-x}As$, whereas the growth rate for metallic alloys is $10^2 - 10^3$ mm/h. The slow growth rate results in large curvature of the interface and cellular growth will be suppressed at such large curvature interface. Instead, polycrystallization and concentration fluctuation are caused when the constitutional supercooling occurrs.

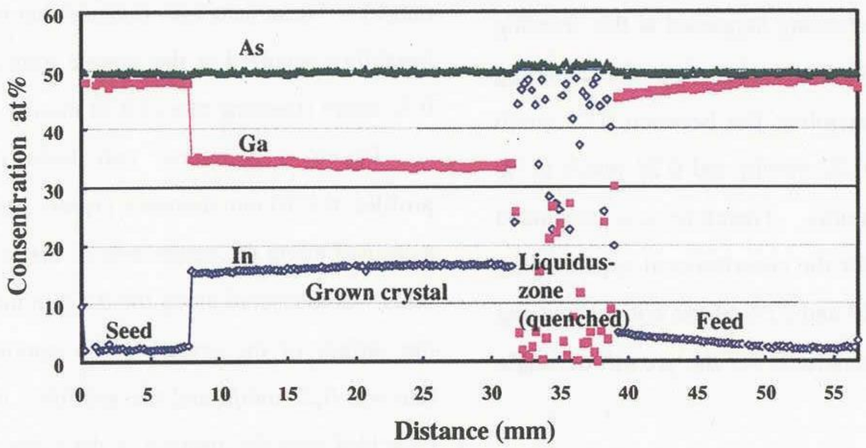

Fig. 3. Compositional profiles of a TLZ grown crystal at a sample translation rate of 0.27 mm/h (23% higher than the critical growth rate).

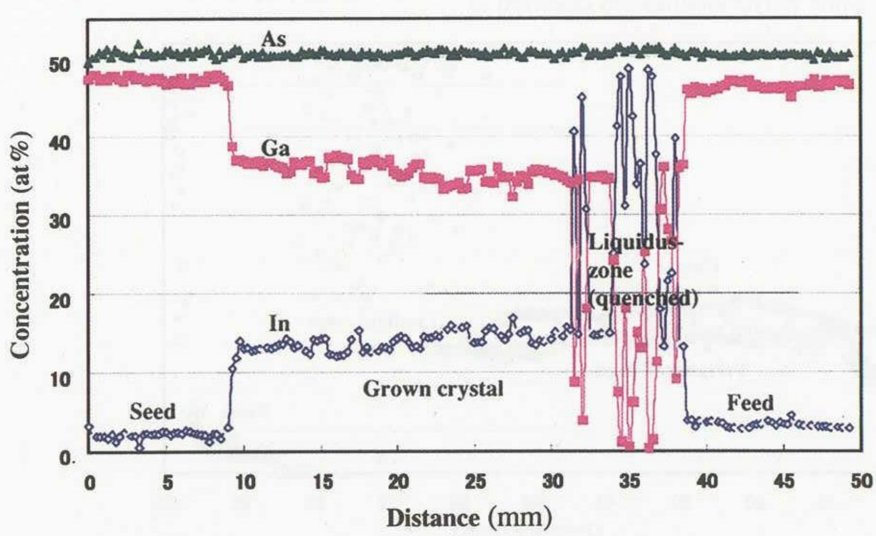

Fig. 4. Compositional profiles of a TLZ grown crystal at a sample translation rate of 0.32 mm/h (45% higher than the critical growth rate).

The real solidified length was compared with the mechanical sample translation distance in this case, too. The result shows that the real solidified length of 24.2 mm was 3.3 mm shorter than the mechanical sample translation distance of 27.5 mm. The real freezing rate, in this case, did not catch up with the mechanical translation rate. This is because the mechanical sample translation rate was 45% higher than the synchronous sample translation rate and was too fast. The real freezing rate was calculated to be 0.28 mm/h based on the grown length and time period for the growth, which is 27% higher than the critical freezing rate. Since the constitutional supercooling happened at this freezing rate, the real critical freezing rate for avoiding constitutional supercooling lies between 0.25 mm/h (14% higher than 0.22 mm/h) and 0.28 mm/h (27% higher than 0.22 mm/h). Therefore, it is concluded that the tolerance for the constitutional supercooling which is between 14 and 27% of the critical freezing rate exists and is beneficial for the growth of single crystals.

Crystallinity of grown crystals is compared in Fig. 5. Single crystallinity is observed when grown at sample translation rate of 0.27 mm/h (freezing rate of 0.25 mm/h), while polycrystallization occurred at the translation rate 0.32 mm/h (freezing rate of 0.28 mm/h). These facts also indicate that the interfacial instability occurred at the sample translation rate of 0.32 mm/h (freezing rate of 0.28 mm/h).

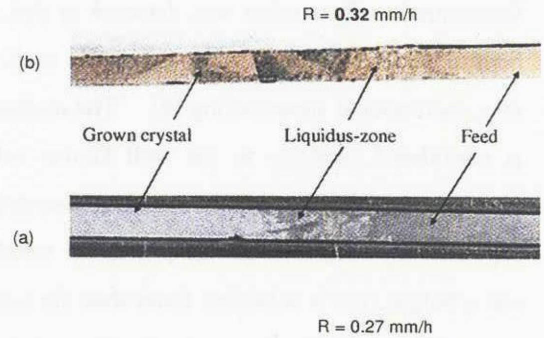

Fig. 5. Cross sectional view of TLZ grown crystals; (a) sample translation rate R = 0.27 mm/h and (b) R = 0.32 mm/h. Polycrystallization occurred at R = 0.32 mm/h.

Figure 6 compares two InAs concentration profiles of a 10 mm diameter crystal; one profile was measured along the center axis of the crystal and the other was measured along the 0.5 mm inner part from the surface of the crystal. The sample translation rate was 0.22 mm/h and the solidified length almost coincided with the distance of the sample translation. It is noted that InAs mole fraction near the surface is about 0.30 but it is about 0.35 in the center and inhomogeneity exists in the radial direction.

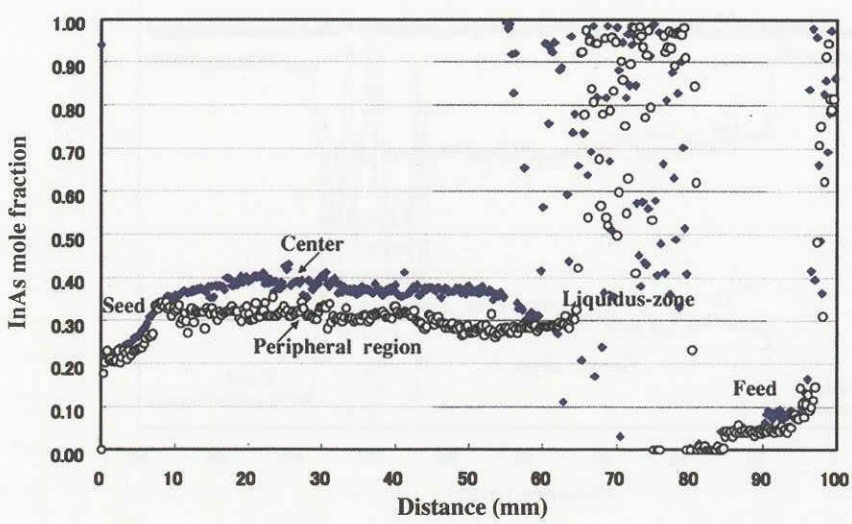

Fig. 6. Compositional profiles of a TLZ grown 10 mm diameter crystal at a sample translation rate of 0.22 mm/h.

Table 1 Relation between the gravity level and the maximum velocity of the convection in a melt

Gravity level	1g		1 μg
Sample diameter (mm)	2	10	10
Maximum velocity (μm/s)	0.4	1×10^{3}	0.003
Degree of supercooling	6×10^{-4}	8×10^{-3}	1×10^{-4}

Moreover, the concentration fluctuates, showing the occurrence of constitutional supercooling. In the case of 2 mm diameter crystal, constitutional supercooling was suppressed up to the freezing rate at least 0.25 mm/h. While, in the case of 10 mm diameter crystal, constitutional supercooling was detected at the freezing rate of 0.22 mm/h even though growth conditions were the same except for diameter difference. When the melt size is increased, the magnitude of convection in a melt will increase. Table 1 compares the maximum convective flow velocity calculated by numerical analysis between 2 and 10 mm diameter in the liquidus-zone during the TLZ growth. In both cases, samples were set parallel to the gravity axis. It is noted that the maximum convective flow velocity is about 2500 times in a 10-mm diameter melt compared with that in a 2-mm diameter melt in 1 g conditions.

These results show that convection in a melt makes the occurrence of constitutional supercooling easier. The local compositional and temperature inhomogeneity in a melt is caused by the convection. Therefore, such local inhomogeneity might increase instability in the crystal growth and caused the constitutional supercooling even at the freezing rate of 0.22 mm/h.

In conclusion, the maximum freezing rate for avoiding the constitutional supercooling in the growth of $In_xGa_{1-x}As$ from its melt was investigated by utilizing constant freezing rate during the growth by the TLZ method. When convection in a melt was suppressed, constitutional supercooling was avoided even at the freezing rate of 14% higher than the critical freezing rate deduced from the Tiller's criteria. This shows that the tolerance for the constitutional supercooling exists. On the other hand, when convection existed in a melt, constitutional supercooling occurred at lower freezing rate. Increase in the local inhomogeneity of solute and temperature distributions in a melt caused by convection might reduce the stability of the growth and might lower the critical freezing rate for avoiding constitutional supercooling.

Summary

The critical freezing rate for avoiding the constitutional supercooling was quantitatively investigated and results showed that the constitutional supercooling occurred at higher growth rate than that predicted by Tiller *et al.* when convection in a melt was suppressed. The real critical freezing rate that experimentally obtained was between 14 and 27% higher than the Tiller's criteria. When convection in a melt existed, the critical freezing rate was reduced below the Tiller's criteria. This might be related to the increase in growth instability caused by local compositional and thermal inhomogeneity in a melt by convection. The quantitative study on the critical growth rate for avoiding constitutional supercooling especially for a semiconductor melt such as $In_xGa_{1-x}As$ is the first.

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