Preparation of InGaAs Starting Materials with the Gradient InAs Concentration

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Preparation of $In_xGa_{1-x}As$ polycrystals having a controlled compositional profile can be realized without occurrence of the constitutional supercooling by using normal directional solidification. Under a high temperature gradient of 40 K/cm at the growth interface, the constitutional supercooling has been successfully suppressed by reducing the growth rate to 0.62 mm/h. From the periodic fluctuation of the composition in the crystal grown from the constitutional supercooling melt, it is supposed that degree of the supercooling becomes maximum in front of the growth interface, where a nucleation and growth abruptly occurs.

1. Introduction

A wide variety of devices can be designed on a multi-component single crystal, in which case an important requirement becomes homogeneity of the composition across the whole crystal. Attempts to grow single crystals having homogeneous composition in space have been limited by melt convection due to the residual acceleration. This drawback can be overcome by using an $In_xGa_{1-x}As$ starting material having a gradient InAs concentration, which compensates the effect of weak melt convection.

Requirements for the starting materials are (1) gradient InAs concentration having a controlled profile, (2) microscopically homogeneous composition free from a constitutional supercooling, (3) precipitation, void and crack free and (4) crystal size of 20mm ϕ x100mml. In order to obtain starting materials satisfying these requirements, we have carried out the investigation using the directional solidification method under various conditions.

2. Experiment

GaAs and InAs polycrystals were charged as row materials in a pBN crucible with a diameter of 32 mm and the crucible was sealed in a quartz ampoule in vacuum. The crystal growth was carried out using a vertical heating furnace shown schematically in Fig. 1. The temperature profile

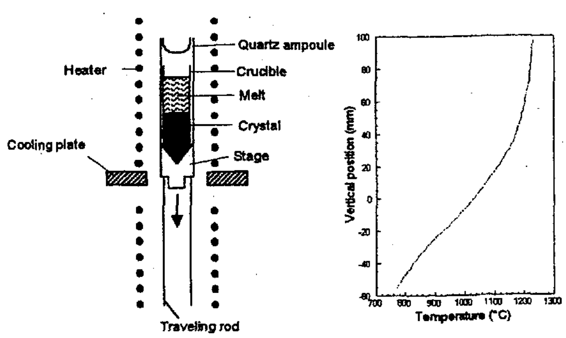

Fig.1 Schematic growth furnace and the temperature profile along the growth axis. A temperature gradient is 40 ~ 60° C/cm.

along the growth axis is also shown in Fig. 1. A temperature gradient of 40~60°C/cm was achieved by using a cooling plate. A large temperature gradient is necessary to prevent constitutional supercooling in the case of such ternary crystal growth. The ampoule was mounted in the furnace and a InGaAs crystal was directionally grown by traveling the ampoule to the lower direction. Growth conditions of each crystals are listed in Table 1. In order to investigate the phenomena of constitutional supercooling and compositional profile, growth experiments under various compositions of the starting melt, traveling rates of the crucible and crystal lengths were performed. Compositional profiles of the grown crystals were investigated using the fluorescent X-ray method and the EPMA method.

In order to evaluate the possibility of growth of a single crystal, seeding experiments were also carried out. Seeding conditions are listed in Table 2. GaAs<100> single crystals were used as seed crystals in all experiments.

Table 1. Growth conditions.

Crystal No.	Starting composition (x value)	Traveling rate of crucible (mm/H)	Length of straight part (mm)
A	0.3	0.62	80
B	0.3	1.24	80
C	0.3	2.00	80
D	0.5	0.62	80
E	0.5	0.62	120
F	0.7	0.62	80

Table 2. Seeding conditions. GaAs<100> crystals were used as seed crystals in all growth.

No.	Composition of melt	Spacer	Result	
			Seeding interface	Periphery
S-1	0.3	not use	single crystal	polycrystal
S-2	0.5	BN powder	micro twin	polycrystal
S-3	0.7	not use	subgrain	polycrystal
S-4	0.3	B_2O_3	single crystal	single crystal

3. Result and discussion

3.1. Constitutional supercooling

Constitutional supercooling is a serious problem in the growth of InGaAs crystals, because the difference of the composition between a liquidus and a solidus of $In_xGa_{1-x}As$ system is large. The constitutional supercooling results in a microscopic fluctuation of the composition and generation of polycrystals. A condition for preventing the constitutional supercooling is generally represented as a ratio of the temperature gradient (G) to the growth rate (R) by the following equation [1].

$$G/R > mC_l(k-1)/kD$$

Where m, C_l, k and D are gradient of liquidus, composition of melt far from the growth interface, segregation coefficient and diffusion coefficient, respectively. According to this equation, the required condition for a stable growth in this system can be estimated to be approximately $G/R > 4.5\times10^6$ Ks/cm^2 assuming the diffusion coefficient of 6×10^{-5}cm^2/s.

Figure 2 shows photographs of vertical cross-sections and compositional profiles measured by the fluorescent X-ray method for crystal A~C, whose starting compositions are 0.3. Compositional profiles are shown by mappings of signal intensities of Ga-K α and line distributions of X-ray intensities from each component at the center of the crystals along the growth direction. Under a condition of small travelling rate of the crucible (crystal A), most of the grains are elongated to the growth direction and the microscopic fluctuation of the composition is hardly observed. While, under conditions of larger travelling rate of the crucible (crystal B, C), discontinuous small grains are generated and characteristic structures are observed in compositional profiles, i. e. phases with low InAs concentrations suddenly appear. Periods of appearance of those phases are 10~15mm and a few mm when travelling rates of the crucible are 1.24 and 2mm/H, respectively. These small grains and phases with low InAs concentrations are attributed to the constitutional supercooling.

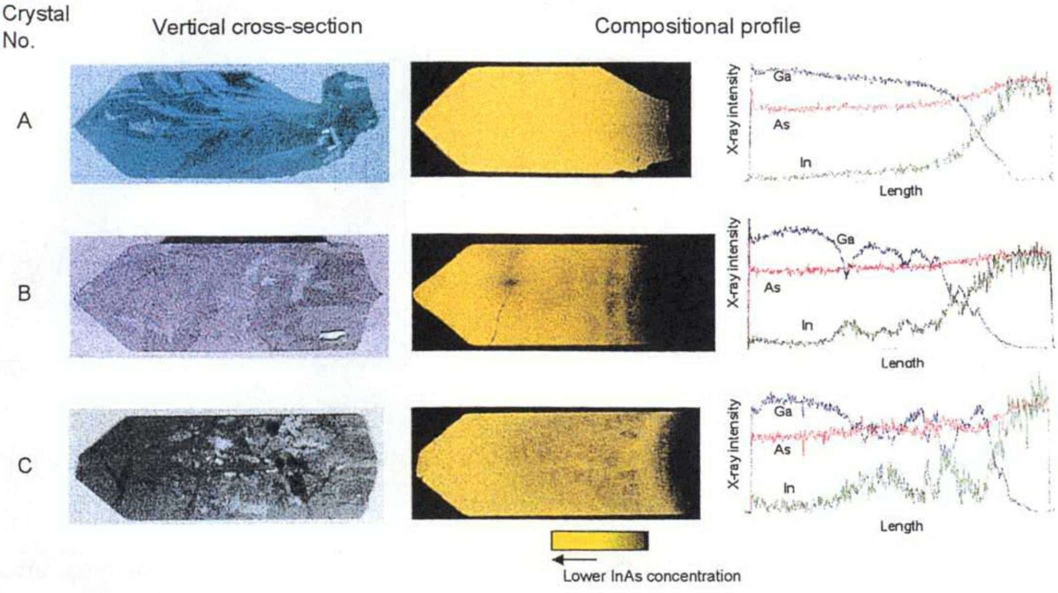

Fig.2 Photographs of vertical cross-sections and compositional profiles measured by the fluorescent X-ray method for crystal A~C. Compositional mappings are drown by signal intensities of Ga-K α . Graphs at the right sides are line distributions of X-ray intensities from each component at the center of crystals along the growth direction.

A cellular structure [2], one of the typical structure which indicates the occurrence of the constitutional supercooling, is not observed in this study. From characteristic structures observed in the compositional profiles, it is probable that a phenomenon schematically shown in Fig. 3 takes place due to the constitutional supercooling. A compositional diffusion layer is generated in front of the growth interface and this diffusion layer becomes supersaturated under the small G/R condition. Then, free nucleations are occurred in the diffusion layer at a position where a supersaturation is maximum. Nuclei grow and a new growth interface is formed. This growth interface is stable till the supersaturation of the melt exceeds the threshold value for the free nucleation. In order to investigate the behavior of the growth interface, we have in-situ measured positions of growth interfaces. Figure 4 shows variations of growth rates calculated from measured positions of growth interfaces under conditions where the constitutional supercooling occurs or not. In this graph the growth rate is normalized by the travelling rate of the crucible. When the constitutional supercooling occurs, the growth rate fluctuates largely. The fact indicates the discontinuous growth due to the constitutional supercooling as mentioned above.

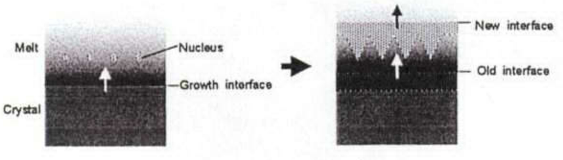

Fig.3 Schematic image of the phenomenon caused by the constitutional supercooling. Arrows at growth interfaces indicate the growth direction. Darker color represents higher InAs concentration.

3.2. Profile of InAs concentration

The most simple method for preparation of the starting materials with gradient InAs concentrations for space experiments is to apply a compositional profile obtained by a normal freezing, which is defined by the directional solidification from completely mixing melt. Figure 5 shows compositional profiles along the growth direction

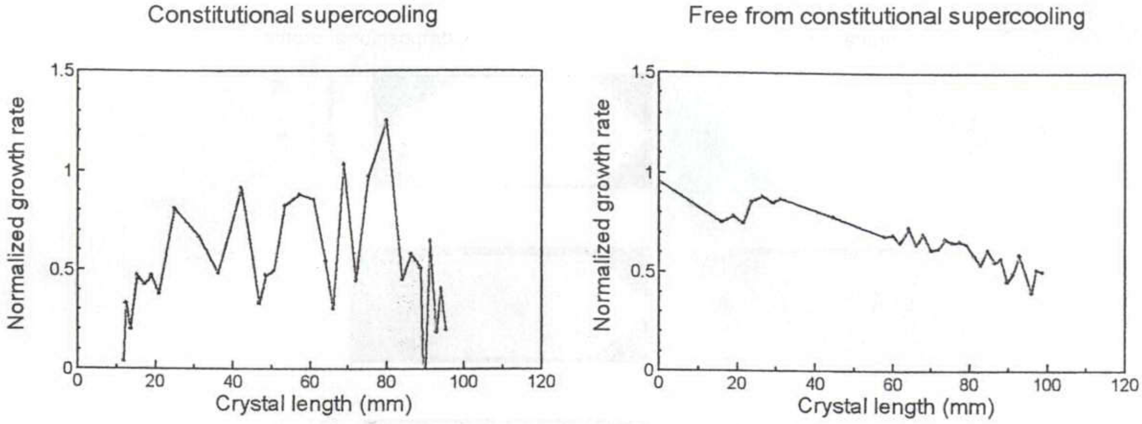

Fig.4 Variations of growth rates calculated from in-situ measured positions of growth interfaces. Growth rate is normalized by the travelling rate of the crucible.

of crystal A, D and F measured by the EPMA method. The horizontal axis indicates a fraction solidified. These crystals were grown under the condition which can prevent the constitutional supercooling. Theoretical profiles calculated assuming the normal freezing for each starting composition are also plotted as solid lines in this figure. Gradient InAs concentrations are found in the compositional profiles of the grown crystals, but these results do not agree with profiles predicted by the normal freezing. InAs concentrations in all experimental results start to increase at smaller fraction solidified than those of theoretical results. The deviation between the experimental and theoretical results is more remarkable in the case of a larger starting composition. These facts suggest that the transport of the solute is dominated by diffusion. In Fig. 2 increase of InAs concentrations indicating an initial transient [3] are clearly observed around the shoulder parts. Furthermore, the generation of characteristic structures due to the constitutional supercooling also suggests the existence of the diffusion layer with a considerable length in front of the growth interface.

In order to confirm the effect of the diffusion in this system, calculations of compositional profiles using the one-dimensional diffusion model have been tried. Calculated profiles assuming the diffusion coefficient of $6\times10^{-5}cm^2/s$ along with the experimental profiles are shown in Fig. 6. The horizontal axis indicates the length. In this graph, the result of crystal E, which has a two times longer straight part than other crystals, is also shown. The experimental and calculated profiles show a qualitative agreement and it is found that the influence of the diffusion on the transport of solute is considerable in the present growth system.

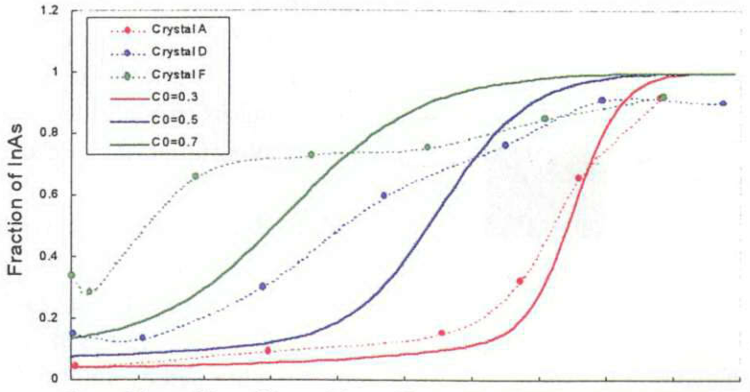

Fig.5 Compositional profiles along the growth direction versus fraction solidified. Solid lines are theoretical profiles with initial composition of 0.3 to 0.7 calculated assuming the normal freezing.

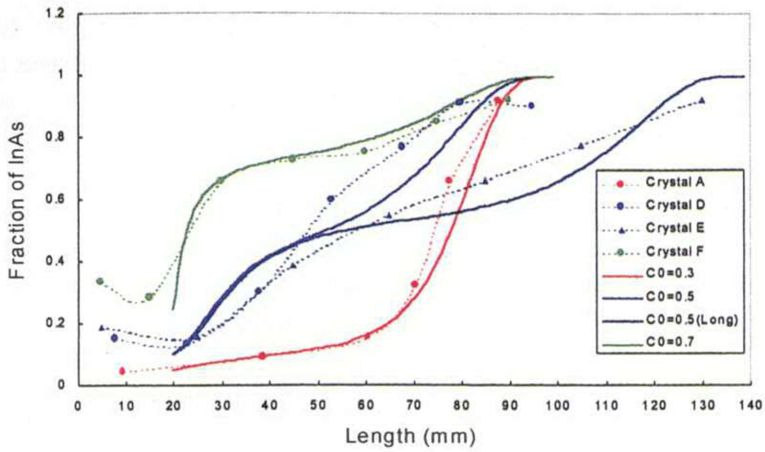

Fig.6 Comparison between the experimental and theoretical compositional profiles. Theoretical profiles with initial composition of 0.3 to 0.7 are calculated using the one dimentional diffusion model assuming the diffusion coefficient of $6\times10^{-5}cm^2/s$.

Camel et al. classified the growth mode using the relationship between log(GrSc) and log(Pe) [4,5]. Where Gr, Sc and Pe are Grasfof, Schmidt and Peclet numbers, respectively. According to that classification, the present growth system with a radial temperature difference of a few °C is classified in the convection limited region, i. e. it is predicted that the growth mode becomes the normal freezing. This analysis is not in agreement with the results of this study. The reason that the diffusive transport of solute can be realized in this growth system seems to be due to the difference of the density between InAs and GaAs melt. InAs melt with larger density swept out of the growth interface forms a stagnant layer at the bottom of the melt.

In diffusion limited growth mode, the formation of the uniform compositional region is expected [3]. But in this study it is not clearly observed, since the initial transient region becomes long due to the small growth rate, which is the necessary condition to prevent the constitutional supercooling as mentioned in the previous section.

3.3. Seeding

In the seeding process in this experiment, there are a few problems. One is that GaAs seed crystals are not lattice matched with the growing crystals. The higher the In concentration of the melt is, the larger the lattice mismatch becomes at the seeding interface. This mismatch induces twins (microtwins) or subgrains at the seeding interface as shown in Table 2. This problem will be solved by using a InGaAs single crystal seed with same composition as that of the crystal grown at the seeding interface. Another problem is invasion of InGaAs melt into the narrow gap between the seed crystal and the wall of the seed holder, which often generates polysrystals at the periphery of seeding interface. The invasion relates to the gap size and the reactivity of InGaAs melt to the seed crystal and the wall. We have tried several methods, such as optimization of the gap size and charge of BN powder or liquid B_2O_3 into the gap. Though B_2O_3 charge gaves better results of single crystal seeding, this invasion has not been reproducibly suppressed yet. Use of InGaAs seed crystal may improve these problems.

3. Summary

By optimizing both the temperature gradient near the growth interface and the growth rate, normal directional solidifications have realized without occurrence of the constitutional supercooling in the $In_xGa_{1-x}As$ system, where x = 0.3, 0.5 and 0.7. It is supposed from the characteristic profiles, i.e. the periodical fluctuation, in both composition and actual growth rate, that the nucleation and growth occurs in the melt region where the degree of the constitutional supercooling is maximum in front of the growth interface.

We confirmed that the compositional profile of an $In_xGa_{1-x}As$ starting material along the growth direction can be controlled by changing the starting melt composition or the crystal length. The compositional profile of InGaAs crystal free from the constitutional supercooling suggests that the transport of solute is dominated by diffusion, since the stagnant of InAs at the bottom of the melt is considered to suppress the convection of the melt.

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