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Constitutional Supercooling during Directional Solidification of $In_{0.3}Ga_{0.7}As$ Melt

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Constitutional supercooling is one of the most important phenomena for crystal growth. There are several theoretical analyses of constitutional supercooling on mixed crystals, but the experimental conditions for occurring constitutional supercooling have not been identified. The constitutional supercooling behavior during directional solidification of a $In_{0.3}Ga_{0.7}As$ melt was investigated by evaluating concentration distribution of solidified samples. The results showed that the limit of sample traveling rate for constitutional supercooling was between 0.9 mm/h and 2 mm/h when the solid liquid (S/L) interface had a temperature gradient of about 40 to 45℃/cm. The pattern of concentration distribution in various traveling rates was also discussed.

1. Introduction

$In_XGa_{1-X}As$ is a promising lattice matched substrate material for laser diodes in communication systems and high mobility devices. By changing the composition, lattice parameters can be changed. Suitable lattice parameters should be selected for the active layer of devices. But in the pseudo-binary system, the liquidus line is far apart from solidus line. So especially for high x value composition, it is very difficult to grow homogeneous single crystals on the ground because high segregation coefficient and convective flow do not allow to keep constant liquid concentration, and cause constitutional supercooling easily. Indeed, growing single crystals of $In_XGa_{1-X}As$ feed supplying CZ method[1,2], and Zone Melting method[3] have been reported, but homogeneous single crystal with high x value remains unsuccessful. Under microgravity environments, crystal growth experiment of $In_{0.05}Ga_{0.95}As$ was carried out in the FMPT[4]. In this experiment, effective segregation coefficient and diffusion coefficient were determined, but a homogeneous single crystal was not obtained.

NASDA has planned to grow homogeneous $In_XGa_{1-X}As$ under microgravity environments using Gradient Heating Furnace (GHF) in Japanese Experiment Module (JEM). Under microgravity environments, as convective flow is suppressed, it is expected that growing single crystals of $In_XGa_{1-X}As$ would be easier than on the ground.

There are several factors that control the growth of single crystal of a ternary semiconductor like $In_XGa_{1-X}As$, such as the solid liquid (S/L) interface shape, the solute concentration at the S/L interface under the residual g environments, quality of a seed crystal, seeding conditions, constitutional supercooling, crucible materials, and so on. Single crystal growth should be carried out under the balance of above factors.

One of the most important points is to avoid the constitutional supercooling to grow single crystals. The theory of constitutional supercooling was established by W. A. Tiller et al.[5]. In general, experimental evaluation of constitutional supercooling is a morphological investigation in which the of S/L interface breakdown from a single crystal is observed. But it is difficult to obtain the suitable single crystal of $In_XGa_{1-X}As$ with high x value at present. So instead of morphological investigation using a single crystal, the concentration distribution of solidified polycrystalline $In_XGa_{1-X}As$ was investigated at various traveling rates and at fixed thermal conditions.

The objective of this investigation is to experimentally determine the condition that causes constitutional supercooling, and to make clear the distribution of concentration caused by constitutional supercooling.

2. Experimental method

Directional solidification experiments of $In_XGa_{1-X}As$ melt were performed on the ground at traveling rates of 0.9, 2.0, 3.0, 4.0, 5.0, 7.5, 10 mm/h at temperature gradients of 30～90℃/cm (which was varied by the sample position and the solidified temperature in the furnace). Starting materials were powders of $In_{0.3}Ga_{0.7}As$ synthesized by Furuuchi Chemical in all experiments.

Polycrystaline $In_{0.3}Ga_{0.7}As$ powder was inserted in a capillary graphite crucible with bore dimensions of $2\times2\times60$ mm^3 and then sealed in a quartz ampoule at about 5×10^{-7} Torr. It is expected to suppress the buoyancy driven convection, since a capillary crucible was used and the upper part of the sample was heated and lower part was cooled.

Quenching experiments were also carried out for samples solidified at traveling rates 0.9, 2.0 and 4.0 mm/h to evaluate the state of solidification. The whole sample device was pulled out of the furnace rapidly and cooled down to room temperature in air ambient.

After solidification, samples were polished and the compositional distribution along the longitudinal direction of the samples was evaluated by line and mapping analyses of electron probe micro-analysis (EPMA) method. Quantitative EPMA analyses were done by using GaAs and InAs standard samples. The probe beam size was about 10 μm in all measurements.

Temperature distribution in the melt was evaluated by measuring the temperature of a dummy graphite sample with the same crucible. We confirmed the temperature distribution was close to the outer quartz ampoule around the position where the sample quenched.

3. Results and Discussion

3.1. Solidification with various traveling rates

All solidification experiments have been successfully carried out. In distributions of the samples measured at intervals of about 250 μm by EPMA line analyses at traveling rates slower than 3.0 mm/h and faster than 4.0 mm/h are shown in Figs. 1 and 2, respectively.

In all the samples, the ratio of atomic percent of In + Ga and As were 1 : 1 from the beginning to more than 90 % length of the samples. In precipitation was observed because of the vaporization of As in the last to freeze part which is less than 10 % of the samples.

Figure 1 shows that In distributions are almost even until about 60 % of solidification and gradually increasing towards the end of solidification. In distribution in figure 1 is considered to follow partial mixing, since the profile can be fitted by partial mixing model[6]. If diffusion coefficient, thickness of diffusion layer and growth rate are assumed to be 1×10^{-8} m^2/s, 4 mm and 2 mm/h, respectively, calculated curve has good agreement with the results of experiments in Fig. 1. From this result existence of diffusion layer in front of the S/L interface is suggested. On the other hand, as shown in figure 2, a considerable scattering in In distributions was observed when traveling rates are faster than 4.0 mm/h. This scattering tends to increase with increasing traveling rates, and is similar to those of the results for directional solidification of $In_{0.5}Ga_{0.5}Sb$[7]. It is suggested that the scattering of data in figure 2 originates from constitutional supercooling as discussed later.

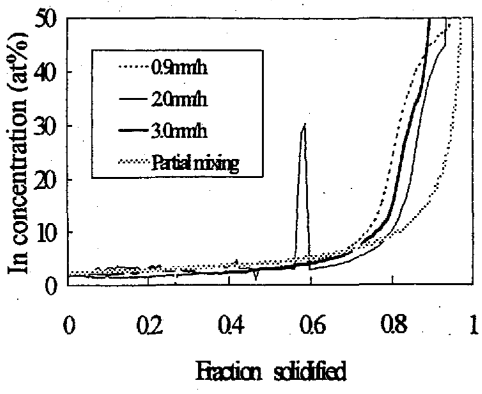

Fig.1 In distributions of samples with traveling rates 0.9 (green), 2.0 (blue), and 3.0 (pink) mm/h, respectively. Fitted curve (red) corresponds to partial mixing.

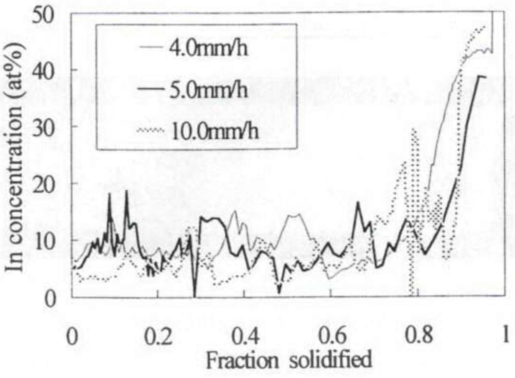

Fig.2 In distributions of samples with traveling rates 4.0 (pink line), 5.0 (red line) and 10.0 mm/h (blue line), respectively.

3.2. Quenching experiments

In order to evaluate the state of solidification, quenching experiments were also carried out for samples with traveling rates 0.9, 2.0, and 4.0 mm/h.

Figure 3 shows the result of a quenching experiment during solidification at a traveling rate of 2.0 mm/h. Every dots is the In concentration evaluated by the EPMA semi-quantitative line analysis at intervals of 10 μ m, and the thick and the thin solid lines are the equilibrium liquidus and solidus line evaluated from the temperature measurements of an outer quartz ampoule and a dummy sample. From these measurements, temperature gradient of the sample at the S/L interface is estimated to be about 43 ℃/cm.

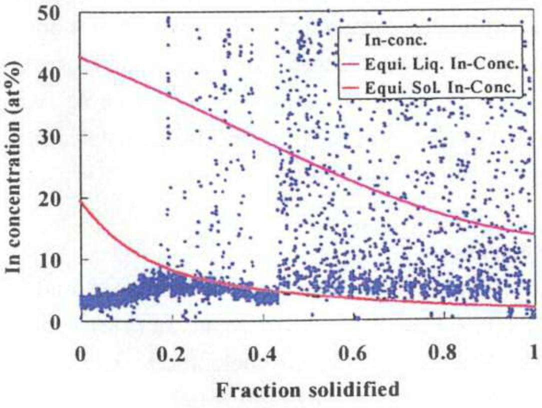

Fig.3 In distribution of the sample quenched on solidifying with traveling rate 2.0mm/h. Every dots are In distribution of the sample. The red and pink line is solidus and liquidus line, respectively.

Diffusion layer was expected to be observed, but diffusion layer of the quenched sample was not observed clearly in this study.

Figure 4 shows Ga distribution of the same sample evaluated by the EPMA qualitative mapping analysis. Higher Ga (lower In) concentration region would be bright and lower Ga (higher In) concentration region would be dark.

From figures 3 and 4, three regions are detected in this sample. Region A, a relatively homogeneous concentration region, was caused by steady solidification. Region C, containing dendritic crystals, is assumed to be caused by a rapid solidification process. This means that this region was molten just before quenching. The last region B, which resembles neither region A nor C, has been caused by nucleation from the crucible wall. This region B shows a steady solidification region just in front of region C.

The results for the sample with traveling rate 4 mm/h was similar to the sample with traveling rate 2 mm/h.

In the region B, there are parts of higher scattered In concentration and lower steady In concentration. The lower In concentration is consistent with that of equilibrium solidus line of the just quench part. Such consistency means that this region was supercooled. It is thought that simple supercooling was not occurred because there had been already steady solidification region and In concentration is less than the starting materials. As the higher In concentration is above the liquidus line, this part was thought to be

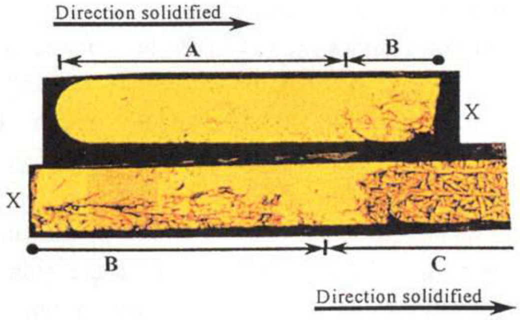

Fig.4 Ga distribution of the sample quenched during solidification at traveling rate 2.0 mm/h.

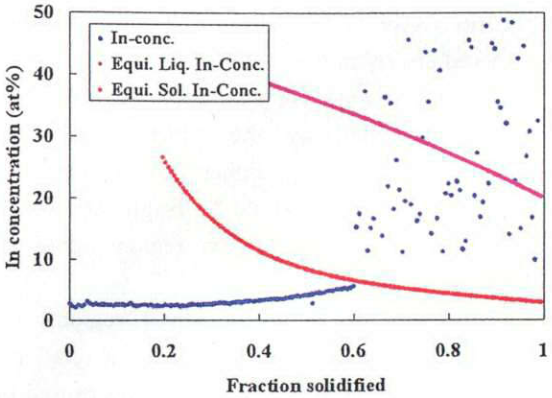

Fig.5 In distribution of the sample quenched during solidification at traveling rate 0.9mm/h. The red and pink lines are solidus and liquidus line, respectively.

liquid just before quenching. So there exists both liquid and solid in this region B, which is a typical feature of constitutional supercooling.

In the same way, the results of quantitative line analysis at intervals of about 250 μ m and qualitative mapping analysis of the quenched sample at a traveling rate of 0.9 mm/h are shown in figs 5 and 6. A region similar to B in figures 3 and 4 is not apparent in this sample. Steady solidification is considered to have occurred at the S/L interface, which intersected solidus line.

3.3 Discussions

The apparent constitutional supercooling seems to occur for samples with traveling rates higher than 4 mm/h judging from In distributions shown in Figs. 1 and 2. However, constitutional supercooling may occur at traveling rates between 0.9 and 2 mm/h. Difference In distribution in quenched samples shows clearly this constitutional supercooling, as compared with Fig. 3 and Fig. 5. At traveling rate lower than 0.9 mm/h, the solidification was fairly steady as shown in figures 5 and 6. At intermediate traveling rate of 2 mm/h, the quenched sample shows steady solidification region A, solid and liquid coexistence region B, and melt region C as a set (Figs, 3 and 4). Coexistence of solid and liquid is an evidence of constitutional supercooling. However, even in such case, if the solid is remelted before the S/L interface reaches the solid, steady state like growth will occur. So in spite of occurrence of constitutional supercooling at traveling rate 2 or 3 mm/h, In distribution is considered to be almost the same.

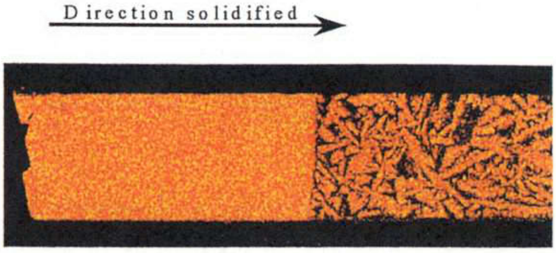

Fig.6 Ga distribution of the sample quenched during solidification at traveling rate 0.9 mm/h.

Such conditions will be fulfilled by the In diffusion towards the solid by the advance of the S/L interface or by the liquid flow due to volume expansion at the solidification.

4. Conclusion

Directional solidification of $In_{0.3}Ga_{0.7}As$ was carried out with various samples traveling rates 0.9 to 10 mm/h. Quenching experiments during solidification at traveling rate 0.9 to 4 mm/h was also carried out. From these experiments constitutional supercooling occurred at temperature gradients about 40 to 45 °C/cm for traveling rate 2mm/h. In this thermal condition, the limit for suppressing constitutional supercooling was experimentally evaluated to be between 0.9 and 2 mm/h. The reason of scattering of the concentration distribution of the sample with traveling rate over 4mm/h was also speculated to be due to constitutional supercooling.

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