# Preparation of InGaAs starting materials having the gradient InAs concentration

Ryu Hirota*, Masami Tatsumi*, Yasuhiro Hanaue** and Kyoichi Kinoshita***

* Itami Research Laboratories, Sumitomo Electric Industries, Ltd.
1-1-1, Koyakita, Itami, Hyogo-Pref., 664-0016 Japan
** Space Utilization Research Center, National Space Development Agency of Japan.
2-1-1, Sengen, Tsukuba, Ibaraki-Pref., 305-8505 Japan
*** Space Utilization Research Program, National Space Development Agency of Japan.
2-1-1, Sengen, Tsukuba, Ibaraki-Pref., 305-8505 Japan

InGaAs starting materials for the crystal growth by the TLZ (Traveling Liquidus Zone) method were prepared by the directionally solidification method. The materials have a macro- and microscopically smooth InAs concentration profile without occurrence of a constitutional supercooling. The samples having nominal In composition(x) of 0.3 were cut from the source materials having x=0.3 - 0.4. Concerning the constitutional supercooling, we have found an evidence for free nucleation ahead of a growth interface from a measurement of microscopic composition profile.

## 1. Introduction

A wide variety of devices can be designed on multi-component single crystals, which are required to have high homogeneity of the composition in the whole crystal. Attempts to grow single crystals having homogeneous composition in space have been limited by still existing melt convection due to the residual acceleration [1,2]. This drawback can be overcome by the TLZ method [3].

Requirements for the starting materials used in the TLZ method are (1) gradient InAs concentration having a controlled profile, (2) microscopically homogeneous composition free from constitutional super-cooling, (3) precipitation, void and crack free and (4) dimensions of 10mmϕ x 100mml. 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 raw materials in a pBN crucible with a 32mm diameter and the crucible was sealed in a quartz ampoule in vacuum. The crystal growth was carried out using a vertical heating furnace schematically shown in Fig. 1. The temperature profile along the growth axis is also shown in Fig. 1. A temperature gradient of 40~60°C/cm was achieved by using the cooling plate. The ampoule was mounted in the furnace and an InGaAs melt was directionally solidified by traveling the ampoule to the lower direction. The grown polycrystal was shaped into 20 mm diameter rod having a cone shape at an end by a rotating

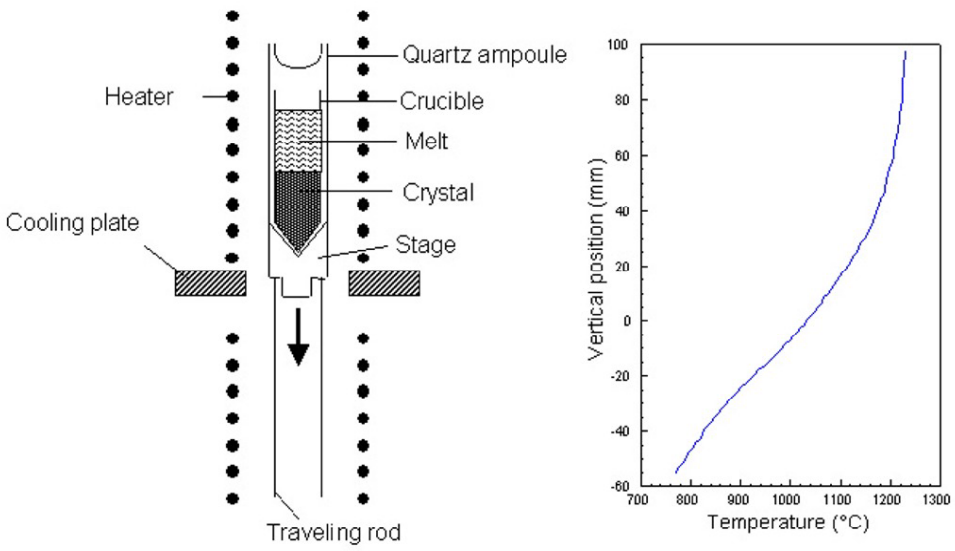



Fig.1 Schematic view of the growth system (a) and the temperature profile measured along growth axis (b).

grindstone. The grain size of diamonds electrically deposited on the grindstone was optimized to 0.1mm. Compositional profiles of the shaped crystals were investigated using the Raman scattering measurement directly on the crystal surface.

A seed crystal should be welded to the cone end in order to grow a single crystal under microgravity. The seed crystal should have a composition of x = 0.3. We carried out preliminary experiment of welding by using InGaAs seed of x = 0.1 and InGaAs crystal of x = 0.7. The junction region was heated to melt locally by an infrared image furnace.

In order to evaluate a possibility of a growth of a single crystal, seeding experiments were also carried out by using a GaAs <100> seed. Use of a boric oxide thin layer on the crucible surface was tried to suppress polycrystalization due to wetting between melt and the wall of the crucible.

In order to clarify the constitutional supercooling in this system, we evaluated the microscopic profile of In at the region of the constitutional supercooling by using the EDX measurement. To elucidate phenomena in crystal growth such as supercooling, it is important to estimate convection and the temperature profile in the melt. We investigated accurate temperature profile in the melt and inside of the crucible.

## 3. Results and discussion

### 3.1. Preparation of source materials having graded In concentration

(A) Synthesis $In_xGa_{1-x}As$ : $In_xGa_{1-x}As$ polycrystals having graded In concentration were prepared by directional solidification of InAs-GaAs solution. In this case it is important to suppress constitutional supercooling, since it generates microscopically large fluctuation of In concentration and modifies the macroscopic concentration profile [1,4]. We certified the constitutional supercooling is stably suppressed

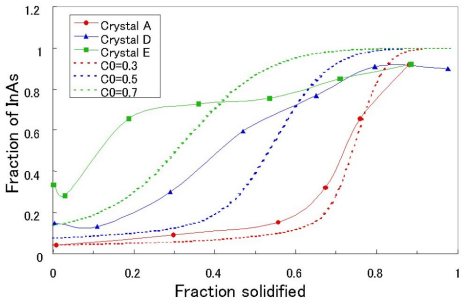



Fig.2 Concentration profile (dashed lines are calculation assuming normal freezing model)

under a solidification rate of slower than 1.0 mm/h in our furnace having a temperature gradient of 40 ºC/cm. Figure 2 shows typical concentration profiles of a solidified InGaAs polycrystal from the raw material of an average concentration of x = 0.3, 0.5, and 0.7, respectively. Nevertheless diffusion and convection coexist in this system, we made it clear that the constitutional supercooling is suppressed under any of the solidification rate mentioned above and the reproducibility of macroscopic In concentration profile is good for each constitution. This concentration profile is applicable even for the newly invented TLZ method by cutting out a crystal from backward. The solidified polycrystals usually had no inclusions and no voids but cracking of the polycrystal often occurred. This cracking originates from the stress due to the variation of the lattice constant in the single crystal grain. (The lattice constant in InAs-GaAs system changes from 0.564 of GaAs to 0.606 nm of InAs. So the cracking occurs in the region of a large variation of the concentration. Therefore it is inevitable to avoid this large stress.) We tried to relax the stress by reducing the grain size, Figure 3 shows as-grown InGaAs starting materials using GaAs powder as a seed, long and slender grains occurred to the growth direction, and any cracks were not found on the outer surface of the crystal.

(B) Raman scattering measurement: It is needed to evaluate concentration profile of the cut out starting materials without varying the shape for the growth in microgravity. We carried out Raman scattering measurements after lapping a crystal slightly. The lapped width was 0.5-1mm and depth was 10-30μm. As a result, we could analyze concentration profiles of a shaped starting material as shown in Fig.4. This small lapped width does not affect a crystal growth.

(C) Welding of a seed crystal: A seed crystal should be welded to the source material for experiments under microgravity since bubbles and

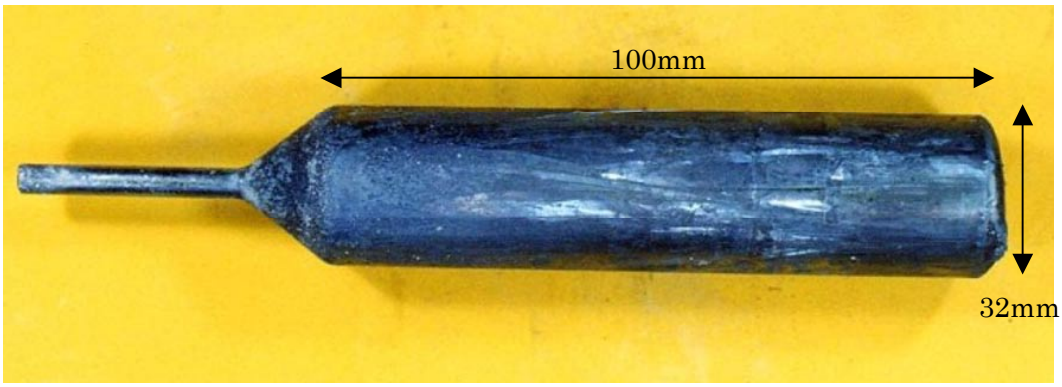



Fig.3 $In_xGa_{1-x}As$ source material having a graded In concentration

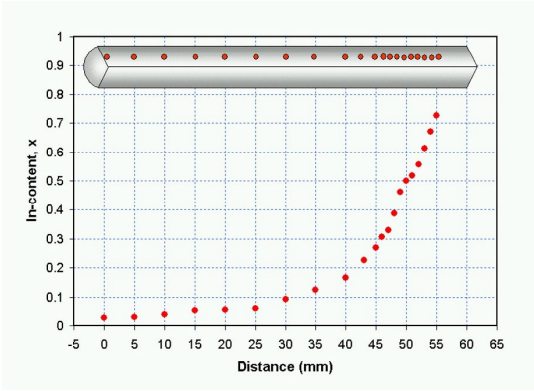



Fig.4 Concentration profile of directionally solidified source material.
The average composition is 0.3.

inclusions made from oxides of the source material cannot be expelled out of the growth interface in the seeding region. Figure 5 shows the preliminary experiment where an InGaAs polycrystal of x = 0.7 rod having diameter of 5 mm was welded to an InGaAs seed of x = 0.1 having the same diameter. Complete welding could not be achieved since it is difficult to keep melt region narrow without dissociation of InGaAs. For preparing a starting material of the TLZ method, it may be worthwhile to insert a thin InAs sheet, in order to reduce the welding temperature.

3.2. Growth of a single crystal

To elucidate the possibility of growing single crystals, we carried out melting experiments with a starting material of average x = 0.3 and a GaAs single crystal as a seed. We used a pBN crucible having diameter of 20mm, and the temperature profile of the furnace was the same as the previous experiment using a crucible of 32mm diameter, and the solidification rate was 0.6mm/h in the VGF mode. As a result single crystals were not obtained since polycrystalization occurred at the seeding interface. The soaking time of 3 hours is considered to be not enough. Figure 6 shows the concentration profile of the grown crystal, it looks as if the whole region of the crystal was melted in the early stage of the crystal growth. This leads to requirement of accurate measurements of temperature profiles in the furnace. So that we have carried out detailed temperature measurements in the crucible and in the melt as mentioned in the next section.

3.3. Constitutional supercooling

(A) Evaluation of constitutional supercooling: Constitutional supercooling originates from a diffusion layer having a concentration distribution in front of a growth interface. Generally cellular structures are formed at the growth interface [5]. In our system no cellular structure was found,

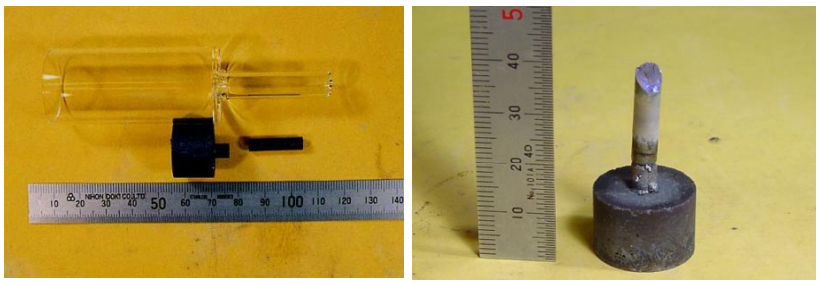
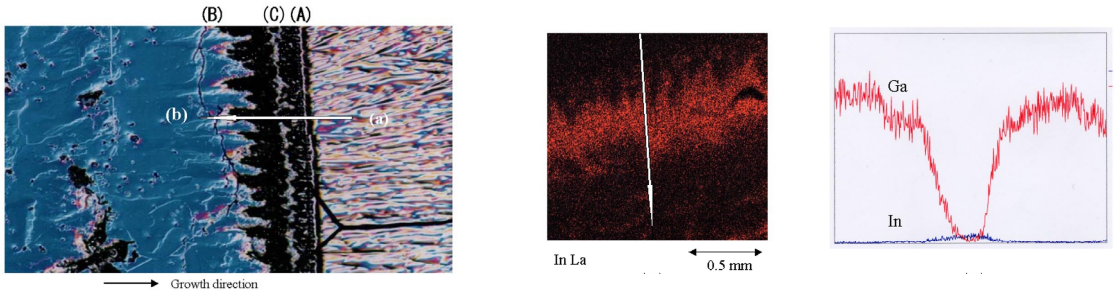


Fig.5 Preliminary experiment of welding a InGaAs ( x = 0.7 ) polycrystal to an InGaAs ( x = 0.1 ) seed


Fig.6 Concentration profile of directionally solidified InGaAs crystal.

though we observed many small grains, microscopically large fluctuations and macroscopically periodic change, of which period was ca. 5 mm, of In concentration. The position of the growth interface changed with corresponding the interval. We have suggested the following model to explain this phenomenon.

Free nucleations occurs 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 free nucleation. From both of this model and the experimental data of periodic change of In concentration, the diffusion layer should be very thick (~5 mm) and the growth rate should give a large effect on the concentration profile. To clarify this model, we have observed the quenched crystal structure continuously and evaluate microscopic concentration profiles of In by the EDX measurement. Figure 7 (a) is a Nomalski microscope photograph of an AB etched surface of the quenched crystal. In front of the grown region where dendrite growth occurred, there is a growth interface (A), a jagged structure (B), and a particular boundary (C) having a small rough structure between (A) and (B). Figure 7 (b) and (c) show microscopic concentration profiles of the same crystal by EDX measurements. The white arrow in (b) corresponds to the same position of the arrow in (a). Along this arrow there is a local maximum of In concentration (red region) between (A) and (B). This result suggests that solidification occurs directionally from both sides of (C), namely,




(a) (b) (c)

Fig.7 (a) Photograph of AB etched surface of constitutional supercooling crystal (b),(c) Concentration profile of directionally solidified source material.

crystal growth occurs from both the regular growth interface and the nuclei ahead of it and (C) is the latest freezed region among (A), (B) and (C) regions.

(B) Temperature measurement: In order to clarify various phenomena such as supercooling in the crystal growth, it is important to elucidate accurate temperature profiles and convection in a melt. Temperature measurements are usually done by setting thermocouples on outer surface of a quartz ampoule or a crucible. In this case, thermocouples would be strongly affected by radiation from heaters and other structures, so that accurate temperature profiles would not be measured. Convection in the melt is estimated by a simulation, for which such inaccurate temperature profiles along wall of a crucible is used for boundary conditions.

To overcome this problem, we carried out temperature measurements shown in Fig.8. To measure temperatures of a pBN crucible itself, straight part of a crucible is inserted into snuggly fitted outer pBN tube and 4 pairs of thermocouples are settled in the gap. To compare these values to the measurement during crystal growth, 7 pairs of thermocouples also settled on the outer side of a quartz ampoule. In order to understand the influence of melt convection, we measured temperature profiles in the melt of different depth. We used a Ga melt instead of an InGaAs melt above GaAs crystal, and 3 pairs of thermocouples were settled at vertically different positions in the center of the crucible.

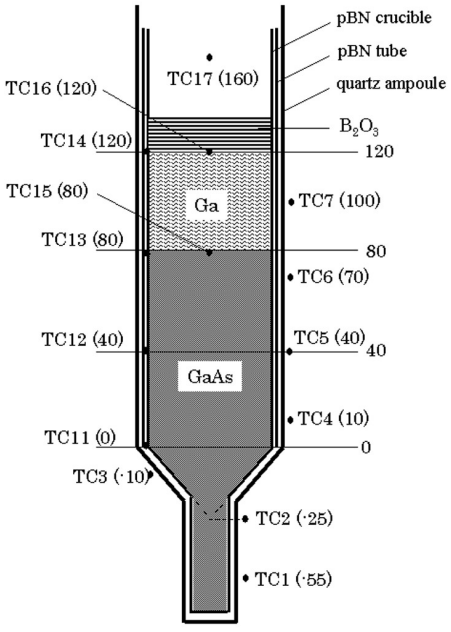



Fig.8 Schematic view of the temperature measurement system

Figure 9 (a) shows temperature measurements when the depth of the melt is 40mm. In this case, all of the thermocouples settled in the center of a crucible were broken because of reaction with evaporated As and Ga. There is a large difference between inside of a crucible and outside of a quartz ampoule. Temperatures of inside of a crucible are uniform by the convection in a melt and the absolute value of it is higher than outside of a quartz ampoule. It leads mistake to use temperatures of outside of a quartz ampoule for simulation. Figure 9 (b) shows measurement when the depth of melt is 80mm. In this case we have succeeded in measuring center of the melt. The abnormal point in crucible position: 630mm is considered to the effect of radiation by the cooling plate. It is shown that the temperature and the temperature profile between center of the crucible and inside of a crucible are almost the same. This result indicates that the convection in the melt is large in this system. It is worthwhile to measure also the crucible position of 120mm to clarify the convection behavior.

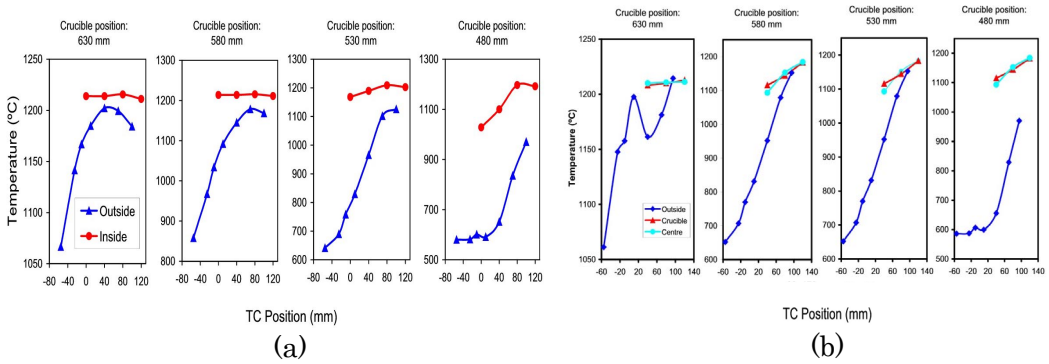



Fig.9 Temperature profiles corresponding to vertical position of the ampoule
(a): depth of the melt is 40mm, (b): depth of the melt is 80mm

## 4. Summary

The polycrystalline source materials for growing a single crystal having uniform composition are prepared by the directional solidification from raw materials having an average composition of x = 0.3 - 0.4. The constitutional supercooling was suppressed. From this material, we have successfully prepared source material for the crystal growth by the TLZ method. The material has an average composition of x = 0.3 and the diameter and the length of straight part are 20 and 100 mm, respectively. We have established a process of the surface treatment for the Raman scattering measurement in order to evaluate In composition profile of this source materials, nondestructively.

Concerning the constitutional supercooling, we have found an evidence for free nucleation ahead of a growth interface from a measurement of microscopic composition profile. We also measured accurate temperature profiles in the crucible for advanced comprehension of solidification phenomena and growth of single crystals.

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