Preparation of InGaAs Starting Materials Having the Gradient InAs Concentration

Masami Tatsumi[†], Hirokazu Kato[††] and Kyoichi Kinoshita[††]

† Itami Research Laboratories, Sumitomo Electric Industries, Ltd. 1-1-3, Shimaya, Konohana-ku, Osaka, 554-0024, Japan

†† Space Utilization Research Center, National Space Development Agency of Japan. 2-1-1, Sengen, Tsukuba, Ibaraki-Pref., 305-8505 Japan

InGaAs starting materials having gradient InAs concentrations were prepared by the directionally solidification method. The materials have macro and microscopically smooth concentration profile without occurrence of a constitutional supercooling. The sample having In composition(x) of 0.3 for growth experiments was cut from the source materials having x=0.4. The microscopic evaluation of In concentration on a region of the constitutional supercooling suggests that free nucleations occur ahead of a growth interface and a new growth interface is formed.

1. Introduction

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

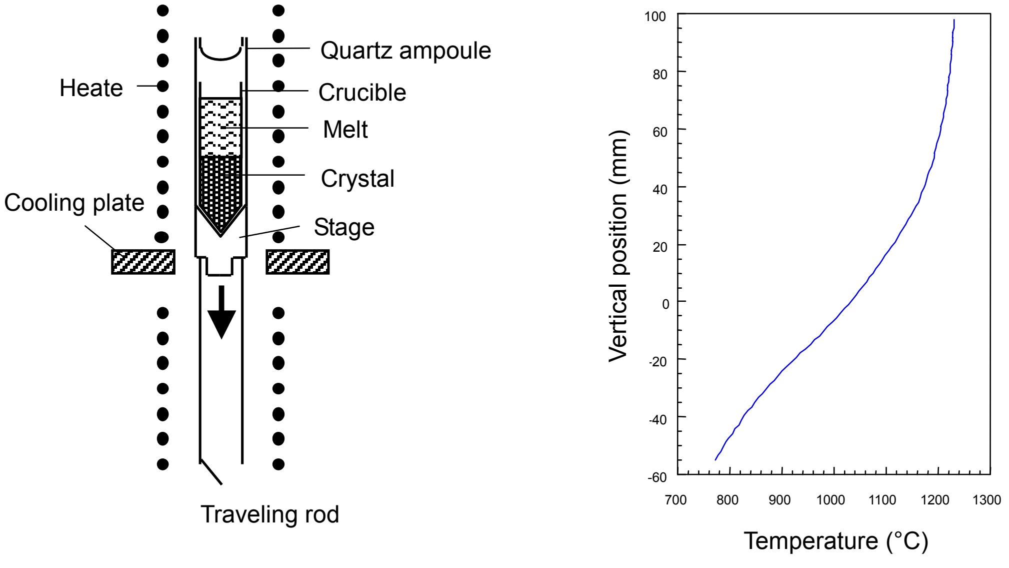
Requirements for the starting materials are (1) gradient InAs concentration having a controlled profile, (2) microscopically homogeneous composition free from a constitutional supercooling, (3) precipitation, void and crack free and (4) crystal size of 20mmφx 100mml. In order to obtain starting materials 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 a InGaAs crystal was directionally grown by traveling the ampoule to the lower direction. Compositional profiles of the grown crystals were investigated using the fluorescent X-ray method and the EPMA method. The grown polycrystal was shaped into 20 mm diameter rod having a cone shape at an end by a rotating grindstone. The grain size of diamond electrically deposited on the grindstone is 0.1~0.2 mm. 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 GaAs seed and polycrystal of x = 0.3. 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 further clarify the constitutional



(a) (b)

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

supercooling in this system, we investigated an effect of the solidification rate on the profile of the concentration and evaluated the microscopic profile of the In at the region of the constitutional supercooling by using the fluorescent X-ray method having a spatial resolution of 10 μm.

3. Result 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 occurrence of the constitutional supercooling, since it generates microscopically large fluctuation of In concentration and modifies the macroscopic concentration profile. We have found that the constitutional supercooling is stably suppressed under a solidification rate of slower than 1.0 mm/h in our furnace having a temperature gradient of 40 ºC/cm. From the previous experiment, this system under the temperature condition is diffusion dominant. The In concentration profiles were reproduced well by a calculated profiles assuming the diffusion coefficient of 6 x 10^{-5} cm^2/s. Figure 2 shows typical concentration profile of solidified polycrystal from the raw material of an average concentration of $x = 0.3$. The reproducibility of this concentration profile is good. In this case no constitutional supercooling was found even in the region of a solidification rate of 1.5 mm/h. The solidified polycrystals usually included no inclusion and no void 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, which was carried out by using GaAs powder as a seed. As the result crack was not found on the outer surface of synthesized crystal.

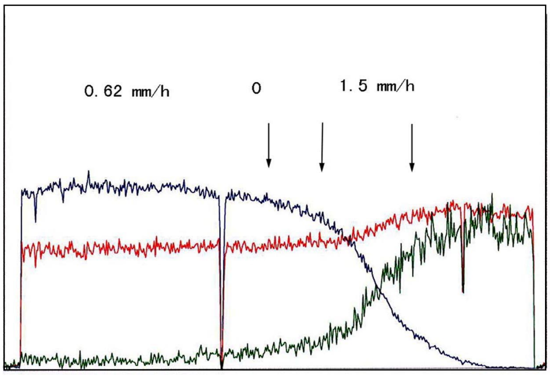


Fig.2 Concentration profile($x = 0.3$)

Seed crystal should be welded to the source material for experiment under microgravity since bubbles and inclusions made from oxides of the source material cannot be expelled out of the growth interface in the seedig region. In the preliminary experiment GaAs seed of 5 mm diameter was welded to the InGaAs polycrystal rod of 5 mm diameter. and melted length was less than 5 mm. Figure 3 is the concentration profile along growth direction in the melted region. The concentration profile shows abrupt change at the junction, which suggests deformation of the concentration profile is hardly occurred by the welding.

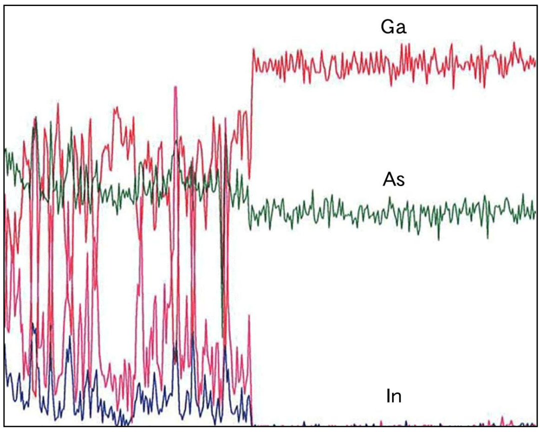


Fig.3 Concentration profile in the welded region of seed.

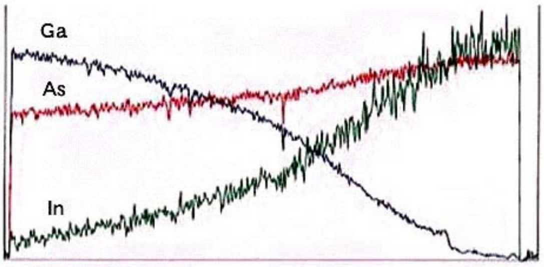


Fig.4 Concentration profile of directionally solidified source material. The average composition is 0.4.

Figure 4 shows concentration profiles of a source material made of directionally solidified crystal from In$_x$Ga$_{1-x}$As melt having an average composition of $x = 0.4$. A photograph of a source material for experiments on earth. cut out of the above material is shown in Fig.5. The diameter is 20 mm and the length of the straight part is about 80 mm. This source material has the average composition of $x = 0.3$ and the graded concentration profile where the In concentration is higher at the seed end. This material was used for a growth experiment on earth.

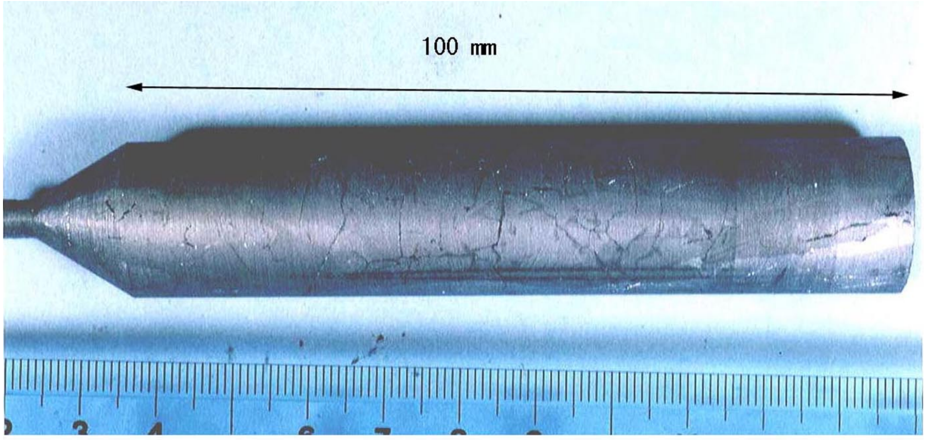


Fig.5 Shaped In$_x$Ga$_{1-x}$As source material having a graded concentration

3.2. Growth of single crystal

We tried to elucidate conditions of growing single crystal by using a GaAs single crystal seed and a starting material of x = 0.3. Though there is a small lattice mismatch between GaAs seed and InGaAs initially growing on it, we can grow a single crystal in a seeding process by adjusting the seeding temperature and the retention time. 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 polycrystals at the periphery of seeding interface. This invasion was suppressed by optimizing the gap size and filling the gap with a small amount of liquid boric oxide. The liquid boric oxide layer on the crucible surface also reduce the wetting between the crucible surface and InGaAs melt. By these improvements, single crystals can be often grown in the region of seeding to 50 mm, where the concentration of In hardly changes along to growth direction. However, polycrystalization is generated in the region where the concentration begins to increase.

To clarify conditions of growing single crystals in the space experiment, we should try to grow from $In_{0.3}Ga_{0.7}As$ single crystal seed and starting material having a graded concentration profile, namely to grow single crystals having a uniform concentration.

3.3. Constitutional supercooling

Constitutional supercooling originates from a diffusion layer having a concentration distribution in front of the growth interface. Generally cellular structures are formed at the growth interface. In our system no cellular structure is found, 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 the corresponding periodic. This phenomenon is may be explained in the following model. 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. From both 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. We changed abruptly the translation rate of the crucible between 0 and 6 mm/h. Any distinct change was not found in the In concentration profile in the crystal, though a small peak of In concentration was observed, which suggests existence of a diffusion layer. Figure 6 shows an AB etched surface of a crystal which reveals a constitutional supercooling. The region corresponds to a boundary region between a regular and a constitutional supercooling region. In the region of the constitutional supercooling there are many grains and irregularities of the concentration and dendrite growth occurrs. Jagged structures are formed along a growth interface in the boundary region(dark region) and the In concentration changes across this boundary. The solution is considered to solidify directionally from both side of this boundary region from the fact that the In concentration shows locally maximum in this boundary region. These results suggest that free nucleations are occurred ahead of a growth interface and a new growth interface.

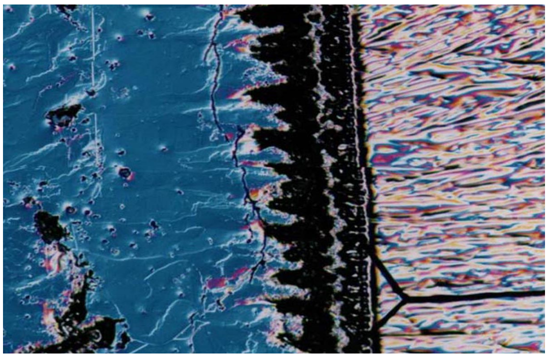


Fig.6 Photograph of AB etched surface of constitutional supercooling crystal

4. Summary

The polycrystalline source materials for growing a single crystal having uniform composition are prepared by a directional solidification from a raw material having an average composition of x = 0.4. The constitutional supercooling was suppressed. From this material, we have successfully made source material for experiments having graded In concentration. 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.

Concerning to an elucidation of a phenomenon on the constitutional supercooling we have found both possibility of existence of a diffusion layer and structures in an AB etching which support the model of free nucleations ahead of a growth interface and formation of anew growth interface.

References

[1] "Elementary Crystal Growth", ed. K. Sangwal (Saan publishers Lublin, 1994).

[2] "Fluid Science and Material Science in Space", ed. H. U. Walter (European space agency, 1987).

[3] W. A. Tiller, K. A. Jackson, J. W. Rutter and B. Chalmers, Acta Met. 1 (1953) 428.

[4] D. Camel and J. J. Favier, J. Crystal Growth 67 (1984) 42.

[5] J. P. Garandet, T. Duffar and J. J. Favier, J. Crystal Growth 106 (1990) 437.