Summary report of the ISS-Kibo utilization mission,
"Growth of Homogeneous SiGe Crystals in Microgravity by the TLZ Method (Hicari)"

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1. Objectives

Objectives of this study are to invent a new homogeneous bulk crystal growth method for solid solutions (mixed crystals) such as Si-Ge and InAs-GaAs using microgravity conditions and to develop the method for practical use. Homogeneous bulk semiconductor crystal growth for solid solutions has been studied for more than 50 years since Shockley invented p-n junction transistors in 1951. If homogeneous mixed crystals are obtained, their energy band-gaps and lattice parameters can be changed by composition and a variety of new devices are made possible in the fields of electronics and optoelectronics. However, no practical growth methods for obtaining device quality mixed crystals have been invented so far. Therefore, if a new growth method is successful, it will contribute to semiconductor industry as well as academic society. In addition, new devices will make our life convenient and comfortable. In those senses, success of this study has a great impact to our society.

2. Experimental methods

In microgravity, convection in liquids can be suppressed. We investigated many growth methods to achieve compositional uniformity utilizing this merit in microgravity. As a result, we invented a kind of zone melting method in which a low melting point material is melted at a relatively low temperature gradient like 10℃/cm and high melting point materials on both sides are remained solid (Patent No. 4239065). In this method, concentration gradient for diffusion-controlled steady-state growth is realized in a melt at the start of crystal growth and homogeneous crystal growth is easy. This is because the solute concentration is saturated in a narrow melt zone and the saturated concentration (liquidus concentration) can be determined uniquely by a given temperature and stable concentration gradient is formed by the imposed temperature gradient. We, therefore, named this new method as a traveling liquidus-zone (TLZ) method. On the ground, convection in a melt stirs the melt and the TLZ method cannot be applied well. Only small diameter crystals or short length crystals can be grown. In microgravity experiments, large and long SiGe crystal growth was tried by suppressing convection in a melt. Moreover, radial growth rate was investigated in detail and two-dimensional growth model was evaluated. Total of four growth experiments were performed in 2013 and 2014. All experiments were carried out at planned growth conditions and all samples were successfully returned.

3. Results

Growth conditions and obtained results are summarized in the table below.

	Planned				Obtained results			
No.	Temp. gradient	Heater velocity	Growth length	Composition	Temp. gradient	Heater velocity	Growth length	Average composition
1	8℃/cm	0.1mm/h	15mm	$S_{i0.5}Ge_{0.5}$	9℃/cm	0.1mm/h	17.2mm	$Si_{0.515}Ge_{0.485}$
2	8℃/cm	0.1mm/h	10mm	$S_{i0.5}Ge_{0.5}$	9℃/cm	0.1mm/h	9.2mm	$Si_{0.502}Ge_{0.498}$
3	8℃/cm	0.1mm/h	15mm	$S_{i0.5}Ge_{0.5}$	9℃/cm	0.1mm/h	14.5mm	$Si_{0.506}Ge_{0.494}$
4	16℃/cm	0.2mm/h	10mm	$S_{i0.5}Ge_{0.5}$	18℃/cm	0.2mm/h	11.4mm	$Si_{0.521}Ge_{0.479}$

Outer view of a space processed sample is shown in Fig. 1. The Si seed, the SiGe grown crystal, the quenched melt, and the Si feed are distinguished. Backscattered electron image of a sample cut parallel to the growth axis is shown in Fig. 2. White striations are observed. These striations show growth interfaces. Such interface marking was made possible by imposing a step-like temperature change by 1℃. Distance between striations and time intervals give precise growth rates. In addition to the axial growth rates, radial growth rates can be calculated by measuring composition on the striations. About 4 times faster growth rate was detected at the initial stage of crystal growth. Such fast growth rate was not observed on the ground. Axial Ge concentration profiles were compared between the #3 and the #4 crystal. Similar concentration profiles were obtained although temperature gradient during crystal growth was different by 2 times. Analysis of this result shows that the growth rate is proportional to the temperature gradient, which agrees well with the TLZ growth model analysis. Obtained results are summarized as follows.

(1) A new crystal growth method named the traveling liquidus-zone (TLZ) method was invented.
(2) Principles of the TLZ growth were confirmed by microgravity experiments, which made clear the growth conditions for large, long and homogeneous SiGe crystals.
(3) A new marking method by the step-like temperature change by 1℃ was successful.
(4) Radial growth rates as well as axial growth rates were determined precisely by measurements of position, composition (solidus temperature), curvature of striations.
(5) Two dimensional TLZ growth rates calculated by the model equation were compared with measured growth rates. Both agreed well at the initial stage of the crystal growth to the distance of 2.3 mm, while difference between the two got larger as crystal growth proceeded.
(6) Growth interface shape changed to flat one and radial compositional uniformity was improved in μG.
(7) About 4 times faster growth rate was observed at the initial stage of crystal growth in μG.
(8) Constitutional supercooling in the TLZ growth and single crystal growth conditions were made clear.
(9) It was found that single crystal growth became easier when weak convection existed in a liquid in the TLZ method. This fact is favorable for the terrestrial growth and for practical use of the TLZ method.

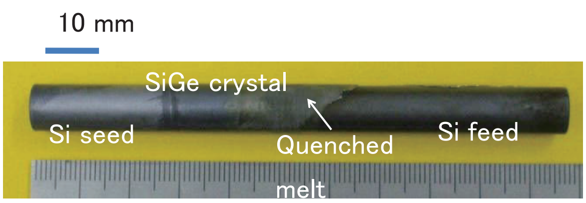

Fig. 1. Outer view of a space processed sample.

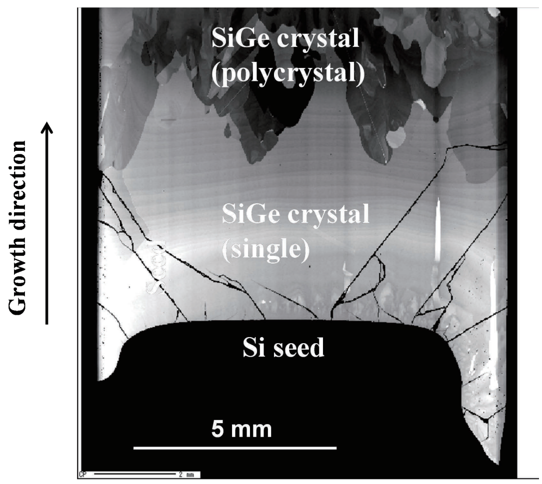

Fig. 2. Backscattered electron image of a sample cut parallel to the growth axis. White striations were imposed by the step-like temperature change of 1℃.

References
1. K. Kinoshita *et al.*, J. Crystal Growth, **388** (2014) 12.
2. K. Abe *et al.* ibid. **402** (2014) 71.
3. K. Kinoshita *et al.*, ibid. **417** (2015) 31.
4. K. Kinoshita *et al.*, ibid. **419** (2015) 47.
5. K. Kinoshita *et al.*, ibid. **455** (2016) 49.