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Growth of SiGe Crystals by the Traveling Liquidus Zone (TLZ) Method - Preliminary Experiments on the Ground -

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Abstract

Preliminary experiments on the ground for the growth of SiGe crystals using a ground model of gradient heating furnace (GHF) are reported. For successful space experiments growth conditions obtained using a laboratory furnace should be transferred to a flight model furnace. However, use of a flight model is limited and a ground model which has similar configuration to a flight model is used for establishing appropriate growth conditions. We noted that temperature profile control using a GHF is more complicated than that achieved in a laboratory furnace since heater length is shorter in the GHF. However by several trials we established appropriate growth conditions. Here we report how we tuned temperature profiles in the GHF and how we established appropriate growth conditions for space experiments.

1. Introduction

Homogeneous $Si_{0.5}Ge_{0.5}$ crystal growth by the TLZ method on board the ISS "Kibo" will be performed in 2011 using a GHF (gradient heating furnace). For compositionally uniform crystal growth, temperature profiles in a furnace are of special importance because growth rate directly depends on temperature gradient as a feature of the TLZ method and composition is determined by the freezing interface temperature. Usually, growth conditions are examined using a laboratory furnace on the ground and optimum growth conditions are determined at a first step. In space experiments, the optimum growth conditions obtained by the laboratory furnace should be realized by a flight model furnace. However, there exists great difference between a laboratory furnace and a flight furnace in many points such as heater length, heat capacity, heat insulation structure and so on. Therefore, to maintain a constant temperature gradient is difficult in a flight furnace. In this paper, procedures for establishing desired growth conditions in the flight furnace and growth of homogeneous $Si_{0.5}Ge_{0.5}$ crystal are described.

2. Experimental Procedures

We chose two temperature gradients 7℃/cm and 14℃/cm for space experiments since temperature gradient 7℃/cm gives growth rate of 0.1 mm/h and 14℃/cm gives growth rate of 0.2 mm/h for $Si_{0.5}Ge_{0.5}$ in the TLZ method and constitutional supercooling can be avoided by these temperature gradients. Then, establishing these temperature gradients in the flight furnace is important. The GHF has three heater zones as shown in **Fig. 1**, an end heater zone, a central heater zone and an auxiliary heater zone. We first determined approximated heater temperatures of each zone using a dummy sample and a Pt – Rd thermocouple; temperatures in a hollow dummy sample were measured by translating a thermocouple. The dummy sample has a structure in which SiN is sandwiched by Si. SiN has high thermal conductivity and was used as a dummy melt zone although it is solid in the test temperature range.

More precise set temperatures were determined by the growth of $Si_{1-x}Ge_x$ crystal. Sample configuration and its relation to a temperature profile in a furnace is shown in **Fig. 2**. A Ge rod ($10mm^{\Phi} \times 20mm^{L}$) is sandwiched by a Si seed ($10mm^{\Phi} \times 30mm^{L}$, <100> orientation) and a Si feed ($10mm^{\Phi} \times 57mm^{L}$), which has low melting temperature and forms a melt zone when it is heated above 938℃. Zone thickness depends on temperature gradient and 25～28mm thick melt zone was formed in the experiments.

If composition of grown crystal is Ge rich the freezing interface temperature is lower than the optimum temperature and in case of Si rich the temperature is higher than the optimum one as is known by the phase diagram. Growth rate V depends on temperature gradient as shown by Eq. (1) in the TLZ method[1-3].

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$$-V = \frac{D}{(C_{L0}-C_{S0})}\left(\frac{\partial C_L}{\partial T}\right)\left(\frac{\partial T}{\partial Z}\right)_{Z=0} \qquad (1)$$

where D is diffusion coefficient between solute and solvent, C_{LO} and C_{SO} are liquidus and solidus concentrations at the freezing interface, $\partial C_L/\partial T$ is reciprocal of slope of the liquidus line, $\partial T/\partial Z$ is temperature gradient. Since D is reported as 9.5×10^{-9} m^2/s by Adachi *et al.*[4] and C_{LO}, C_{SO} and $\partial C_L/\partial T$ are obtained from phase diagram of the Si – Ge system[5], temperature gradient in the zone is deduced if we know the growth rate *V.* Thus deduced temperature gradients were compared with those expected by set temperatures. Then, set temperatures were adjusted for establishing desired temperature gradients.

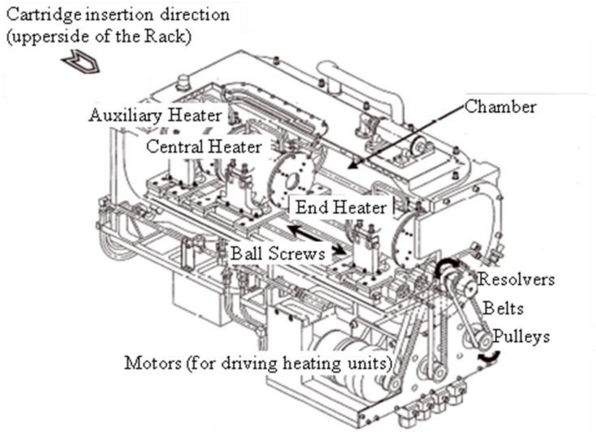

Fig. 1 Schematic view of a gradient heating furnace (GHF)

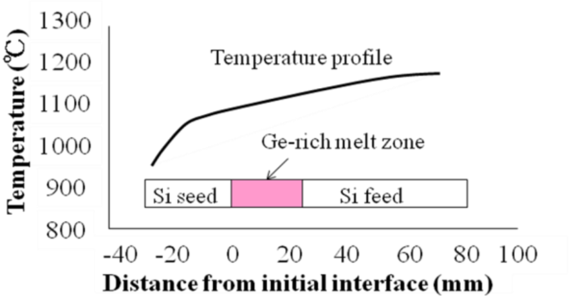

Fig. 2 Schematic view of sample configuration and its relation to temperature profile in a furnace.

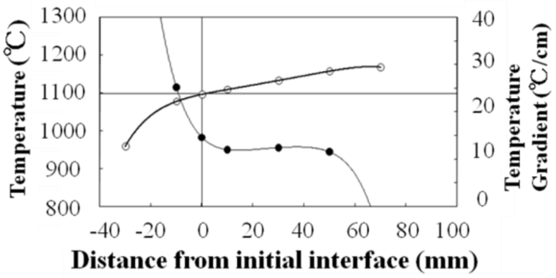

Fig. 3a An example of temperature profile measured in a dummy sample at a start position, open circles denote temperatures and solid circles denote temperature gradients.

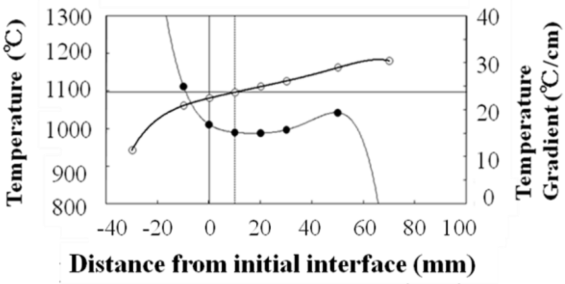

Fig. 3b An example of temperature profile measured in a dummy sample at an end position, open circles denote temperatures and solid circles denote temperature gradients.

3. Results and Discussion

3.1 Temperature Profiles in a Dummy Sample

An example of measured temperature profile in a dummy sample is shown in **Fig. 3a** by open circles. Temperature gradient was set to be 14℃/cm. Dependence of temperature gradient on the position is shown by solid circles (see the right hand ordinate for their values). This temperature profile was obtained at the start position of three heaters. Since heater length is small, temperature profile change due to heater translation is rather great. Temperature gradient is very important factor in the TLZ method since it determines growth rate. Therefore constant temperature gradient throughout crystal growth is desirable. Temperature profile after 10mm translation of heaters is shown in **Fig. 3b**. Temperature gradient changed to large extent in higher temperature zone although temperature gradient at the freezing interface is almost fixed constant.

3.2 Experiment based on Measured Temperatures

A SiGe growth experiment was performed in the temperature profile described above. A 13mm long crystal was grown and it was polycrystalline. Ge concentration profiles of the grown crystal are shown in **Fig. 4**. In the figure, upper image is two dimensional mapping of Ge concentration and concentration change is shown by a different color. In the grown crystal region, Ge concentration increased abruptly to about 0.4 mole fraction. Such lack of initial transient region is characteristic to the TLZ method because initial freezing temperature can be adjusted in the TLZ growth. After 13mm growth, Ge concentration fluctuates. This region was melt zone during crystal growth. Fluctuation of Ge concentration was caused by dendrite growth of Si-rich crystals from a melt in the cooling process.

We aimed at the growth of a homogeneous $Si_{0.5}Ge_{0.5}$ crystal but initial composition was $Si_{0.6}Ge_{0.4}$ and it changed to $Si_{0.65}Ge_{0.35}$ at the end of the growth. Growth rate was measured to be 0.3mm/h and 1.5 times larger than predicted one. Composition and growth rate differences come from temperature profile difference between a predicted profile and a real one. This may be natural because temperature profiles were measured using a dummy sample. Real temperature profiles in a sample should be different due to thermal conductivity difference between a dummy sample and a real sample. The important point is temperature profile tuning after the growth experiment. Judging from measured compositional profiles, initial freezing temperature was about 60℃ higher and 90℃ higher after 13mm growth. Temperature gradient may be 1.5 times higher than expected and is assumed to be about 21℃/cm.

3.3 Temperature Adjustment

Based on the results of the first experiment, set temperatures were adjusted so that the freezing temperature at a start position of the heater is 60℃ lower. Heater translation rate was set at 0.3mm/h. A 4mm long single crystal was grown in this case. Obtained concentration profiles are shown in **Fig. 5**. Crystal composition at the initial freezing interface is about S$_{i0.47}$Ge$_{0.53}$ and it is closer to Si$_{0.5}$Ge$_{0.5}$ than the first experiment owing to temperature adjustment Compositional homogeneity is also observed to be much improved. If initial temperature is raised about 10℃, composition close to Si$_{0.5}$Ge$_{0.5}$ will be obtained.

3.4 Determination of Experimental Conditions

According to procedures described above set temperatures in a ground model of a GHF were determined so that Si$_{0.5}$Ge$_{0.5}$crystals are to be grown at the start of crystal growth. Temperature gradients planned in space experiments are 7 and 14℃/cm and set temperatures were also adjusted to establish these values and to maintain constant temperature gradients for realizing homogeneous composition of Si$_{0.5}$Ge$_{0.5}$ because growth rate depends on temperature gradient in the TLZ method and it requires constant temperature gradients.

Compositional profiles obtained by the ground model furnace at a temperature gradient of 7℃/cm are shown in **Fig. 6**. It is shown that compositionally homogeneous Si$_{0.5}$Ge$_{0.5}$ crystal is grown. Si and Ge concentrations are 50 at% and both data are almost on the same line. Thus, compositional homogeneity reached the same level as that obtained by a laboratory furnace.

Adjacent to a Si seed, about 5mm long single crystal was grown and polycrystallization occurred. Occurrence of polycrystallization may be caused by constitutional supercooling.

4. Plan for Space Experiments

We established homogeneous SiGe crystal growth conditions for a ground model furnace. Although this furnace is similar to

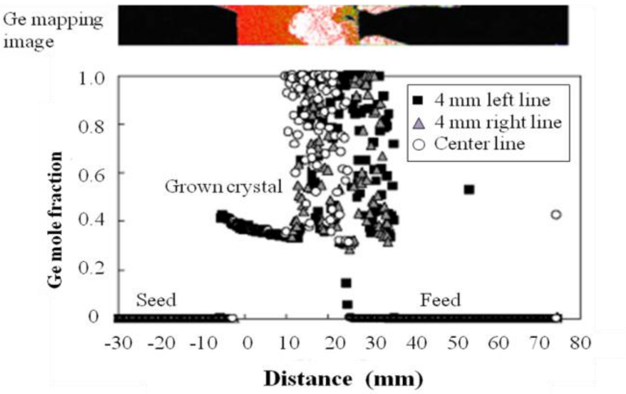

Fig 4 Ge concentration profiles in the growth direction and two dimensional mapping of Ge concentration (above)

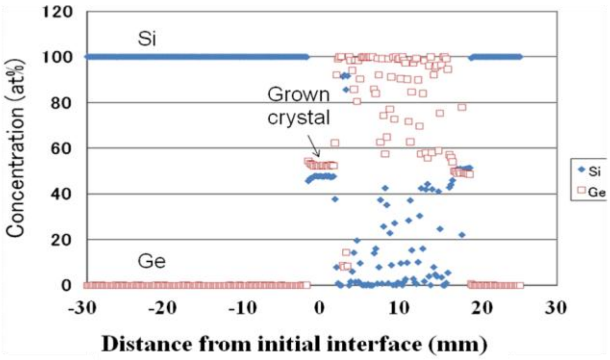

Fig. 5 Adxial compositional profiles of a SiGe grown by a second run.

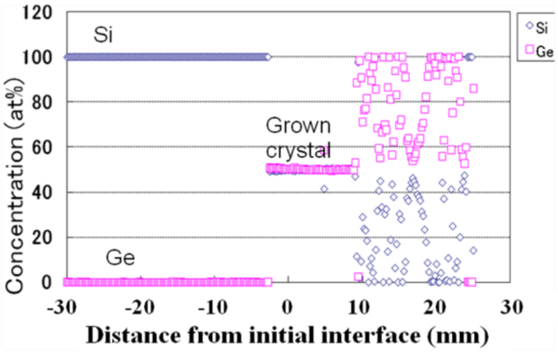

Fig. 6 Adxial compositional profiles of a SiGe grown by ajusted temperature profiles.

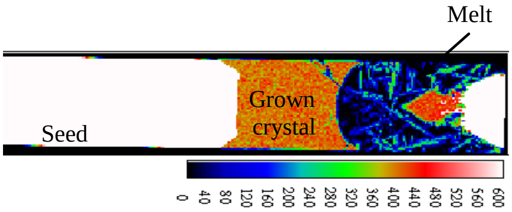

Fig. 7 Two dimensional mapping of Ge concentration

the flight model furnace in heater configuration and heater length, it is not the same as the flight model furnace. Therefore, some adjustments are necessary in space experiments such as initial set temperatures of three heater elements and set temperature variation in accordance with heater translation. We are planning heater set temperature adjustment according to two procedures. One is temperature profile measurements using a dummy sample in space. Another procedure is compositional analysis of a space-grown sample. Therefore, one sample among four will be returned to the earth prior to three space experiments. One of merits of International Space Station utilization is repeated experiments and we will utilize such merits fully.

The aim of space experiments is to evaluate 2 dimensional model of the TLZ method which is expressed by Eq. (2).

$$-\frac{\partial f}{\partial t}=\frac{D}{(C_L-C_S)}\frac{\partial C_L}{\partial T}\left(\frac{\partial T}{\partial Z}-\frac{\partial T}{\partial r}\frac{\partial f}{\partial r}\right) \tag{2}$$

where $\partial T/\partial r$ is radial temperature gradient and $\partial f/\partial r$ is interface curvature as shown in **Fig. 7.** Comparing to one dimensional model equation, a term $(\partial T/\partial r)\times(\partial f/\partial r)$ is introduced in Eq. (2). When crystal diameter gets large, effects of radial temperature gradients on compositional homogeneity become large and this term cannot be ignored. For obtaining large homogeneous crystals by the TLZ method two dimensional effects should be quantitatively evaluated. On the ground, convection in a melt hinders correct evaluation of this term. In microgravity convection in a melt is suppressed and we can evaluate two dimensional term quantitatively by the compositional analysis of space grown crystals. Constitutional supercooling can also be suppressed in microgravity because local solute concentration fluctuation can be suppressed without convection in a melt.

5. Summary

We established homogeneous SiGe crystal growth conditions by the TLZ method using a ground model furnace. In space experiments, establishment of growth conditions using a flight model furnace will be performed by similar procedures to those reported here; temperature profile check by a dummy cartridge and set temperature adjustment after one crystal growth experiment.

Objectives of microgravity experiments are evaluation of two dimensional TLZ growth model and to obtain basic data for growing large homogeneous alloy crystals by the TLZ method on the ground.

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