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Growth of Si$_{0.5}$Ge$_{0.5}$ Single Crystals by the Traveling Liquidus-zone Method and their Structural Characterization

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Abstract

We have succeeded in growing compositionally homogeneous Si$_{0.5}$Ge$_{0.5}$ crystals with a newly developed growth method named the travelling liquidus-zone (TLZ) method. In this method, a narrow liquidus-zone saturated by a solute is formed at relatively low temperature gradients, 5 – 15 °C/cm. Since the solubility depends on temperature, solute concentration gradient is established at the freezing interface. The concentration gradient causes diffusion of the solute towards a low concentration side. At the freezing interface, crystal growth proceeds due to the decrease in solute. As a result, solute concentration increases at the opposite side of the zone by transported solute and part of the remaining feed is dissolved. Thus, the zone travels under the temperature gradient spontaneously. Here, we report on 30 mm diameter homogeneous Si$_{0.5}$Ge$_{0.5}$ crystal growth by the TLZ method. Compositional homogeneity of grown crystals was excellent but the length of single crystal was limited to about 2 mm and origins of polycrystallization were discussed.

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1. Introduction

Performance of electronic devices has been improved to meet market demands for low power consumption and high speed by the scaling down of their line-width. As the line-width is reduced to 30 nm, scaling down, however, approaches its limit. We were focused on the growth of SiGe single crystals to overcome limitations of silicon technology, because both strained Si and Ge films grown on SiGe substrates have higher mobilities than intrinsic Si and Ge, which indicates that the Si$_{0.5}$Ge$_{0.5}$ promises as a substrate material for electronic devices. However, the growth of homogeneous crystals is very difficult, because convection in a melt combined with segregation causes compositional variation in a grown crystal. Therefore, we invented a new growth method and succeeded in growing compositionally homogeneous Si$_{0.5}$Ge$_{0.5}$ crystals. Here, we report the results of crystal growth by the TLZ method.

Figure 1 shows the principle of the TLZ method by referring to the growth of Si$_{0.5}$Ge$_{0.5}$. In the method, a melt zone is formed by melting Ge sandwiched by solid Si at relatively low temperature gradients (5-15 °C/cm). The molten Ge dissolves adjacent Si and the molten zone is saturated by Si and liquidus zone is formed. In such configuration, zone travels towards higher temperature side due to the interdiffusion between Si and Ge. The zone travelling rate $R$ is given by Eq. (1) based on our one-dimensional TLZ growth model.

$$ R = -\frac{D}{C_L-C_S} \left( \frac{\partial C}{\partial T} \right) \left( \frac{\partial T}{\partial z} \right) \bigg|_{z=0} $$

where $D$ is the interdiffusion coefficient between the solute and solvent, $C_L$ and $C_S$ are solute concentrations in a liquid and in a solid at the freezing interface, respectively. $\partial C/\partial T$, $\partial T/\partial z$ and $z$ are reciprocal of the slope of the liquidus line, temperature gradient, and distance measured from the freezing interface, respectively.

2. Experimental

Starting materials composed of a Si seed, a Ge zone forming material, and a Si feed were inserted into a boron nitride crucible with diameter of 30 mm. The crucible was then sealed in vacuum in a quartz ampoule. This ampoule was set in a horizontal temperature gradient furnace and was heated so that the interface temperature between the Si seed and Ge was about 1098 °C for Si$_{0.5}$Ge$_{0.5}$ crystal growth. The highest temperature in the furnace was below 1190 °C so as to avoid softening of a quartz ampoule. As the liquidus-zone travels to the lower Ge concentration side (towards the higher temperature side) due to the interdiffusion between Ge and Si, the ampoule was translated towards the lower temperature side at the freezing rate $R$ as calculated by Eq. (1) in order to maintain the same position of freezing interface relative to the furnace. Orientation of grown crystals was <100>. The grown crystals were first cut parallel to the growth axis and then roughly polished and they were checked whether the grain boundary exists or not. Then, they were mirror polished and their compositional profiles were measured using an electron probe micro analyzer (EPMA). Detailed analysis of crystallographic orientation was performed using electron back scattering pattern (EBSP).
3. Results and discussion

3.1 Homogeneous crystal growth

Figure 2 shows outer view of a grown crystal. As shown in Figs. 3, 4, 5, and 6, we have succeeded in growing compositionally homogeneous Si$_0.5$Ge$_{0.5}$ crystals on a Si-seed with 30 mm diameter. The way of obtaining homogeneous crystals is to match the translation rate of a crucible to the zone traveling rate $R$. When this condition is fulfilled, freezing interface position relative to the temperature zone in a furnace can be fixed and the freezing temperature can be kept at a constant value, resulting in compositional uniformity. In the experiment, after about 7 mm long crystal growth, the sample was cooled. The zone traveling rate $R$ was 0.16 mm/h at a temperature gradient of 10 °C/cm. This rate agrees well with the calculated rate$^4$ using Eq. (1) when the Si-Ge interdiffusion coefficient is $D = 9.5 \times 10^{-9}$ m$^2$/s.
Fig. 3. Optical micrograph of the a-a’ cross-sectional surface of the grown crystal.

Fig. 4. EPMA two dimensional l mapping image of the crystal shown in Fig. 3.

Fig. 5. Si and Ge concentration profiles along the center axis for a 30 mm diameter crystal.
3.2 Crystalline structure of the grown crystal

Figure 7 shows an EBSP image of another crystal cut parallel to the growth axis. The red region shows crystallographic <100> orientation. The seed/crystal interface lies left end of the image. A crystal which took over the seed orientation grew on the seed. However, polycrystallization occurred at a distance of about 2 mm away from the seed/crystal interface. In order to investigate the mechanism of polycrystallization in more detail, the grown crystal was cut perpendicular to the growth axis. In Figs. 8(a) ~ (c), EBSP radial mapping images at various distance from the seed/crystal interface are shown. Figure 8(a) shows that <100> oriented area extends almost the whole of the sample but polycrystallization seems to occur from the arc side. The arc contacted wall of a crucible. Therefore, polycrystallization seems to begin at the crystal surface which contacts a crucible. Figures 8(b) and 8(c) clearly show that polycrystallization progresses from the arc side to the inner of the sample.

When we consider origins of polycrystallization, two main factors are included; one is lattice mismatch between a seed and a grown crystal and the other is constitutional supercooling inherent to the alloy system. As shown in Fig. 8(a), at the seed/crystal interface a single crystal that took over the seed orientation began to grow. This fact excludes the polycrystallization caused by lattice mismatch. In fact, 20 mm long Si0.5Ge0.5 single crystals were grown by the TLZ method for 2 mm diameter crystals. The important fact is that a single crystal changed to polycrystals according as the crystal growth proceeded for 30 mm diameter samples. Since the constitutionally supercooled region is formed ahead the freezing interface, polycrystallization due to constitutional supercooling may consistent with the observed result. It should be further noted that local inhomogeneous distribution of Ge or Si due to convection will increase degree of constitutional supercooling. As for the strength of convective driving force, Grashof number $G_r$ defined by Eq. (2) gives order of magnitude where $g$ is gravity acceleration, is volume expansion coefficient of a melt, $T$ is a temperature difference between the two ends of a melt, $L$ is characteristic length of a melt and is kinematic viscosity of a melt.

$$G_r = \frac{g\beta\Delta TL^3}{\nu^2}$$

Comparison of convective driving force between 2 and 30 mm diameter melts, convection in a 30 mm diameter melt gives 3 orders of magnitude higher than that in a 2 mm diameter melt. It should be
reasonable that local inhomogeneity due to convection was suppressed in 2 mm diameter crystals and constitutional supercooling was avoided, which resulted in long single crystal growth. Then the most probable origin of polycrystallization of large diameter crystals is considered to be constitutional supercooling. Results of Figs. 8(a) ~ (c) show importance of suppressing convection in a melt for avoiding polycrystallization due to constitutional supercooling. In order to grow large bulk Si$_{0.5}$Ge$_{0.5}$ single crystals, appropriate temperature profile, stabilization of the growth interface temperature and avoidance of constitutional supercooling by suppressing convection in a melt are required. In the present experiments, horizontal arrangement for crystal growth was adopted. However, vertical arrangement is more stable for convection if higher density materials are set below the low density materials. Crystal growth using a vertical temperature gradient furnace and stabilizing density difference are expected.

Fig. 7. EBSP mapping image parallel to the growth axis.
Fig. 8. EBSP mapping images perpendicular to the growth axis: ~0.3 mm away from a seed (a), ~0.8 mm away from a seed (b), ~1.4 mm away from a seed (c).

4. Summary

We have invented the travelling liquidus-zone method for obtaining homogeneous Si$_{0.5}$Ge$_{0.5}$ crystals. Large diameter crystals such as $d=30$ mm and 5 mm long homogeneous crystals with single crystal grains of about 2 mm length were grown. The growth of such homogeneous crystals has been accomplished for the first time. Further study for single crystallization of large diameter crystals is being undertaken.

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