Detailed Results of This Period

Growth of Homogeneous Si$_{0.5}$Ge$_{0.5}$ Single Crystals by the Traveling Liquidus-Zone Method

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Abstract

We have challenged the Si$_{0.5}$Ge$_{0.5}$ bulk crystals growth. Si-Ge homogeneous single crystals are difficult to grow so far. In the present research, we have applied the Traveling Liquidus-Zone method (TLZ method) which was invented in our group as a new crystal growth method to the growth of Si-Ge. The diameter of grown crystal was 2mm and the length was 15mm. Crystals were well seeded and had the orientation of silicon seeds in spite of the large lattice mismatch. The compositional variation of the crystals was very small and the composition was in the mole fraction range of 0.5±0.016 in germanium. The lattice constant determined by the X-ray powder diffraction was 55.38nm.

1. Introduction

A large number of studies on SiGe have been done energetically because SiGe thin film[1-4] is expected higher speed[5-7], lower noise[8] and lower electric power consumption compared with the existing device of Si series.

However, few investigations on the bulk crystal growth of SiGe have been done because the growth of homogeneous crystals was very difficult by the existing techniques[9, 10].

In this study, we tried to grow homogeneous Si$_{0.5}$Ge$_{0.5}$ crystals by the TLZ method, and evaluated the quality of grown crystals.

2. Traveling Liquidus-Zone method

We explain here the TLZ method briefly by using our previous experimental results in the InGaAs system.

InAs and GaAs bulk crystals, which are sealed in vacuum in a qualtz ampoule, are set in an electrical furnace having a temperature gradient so as to form the liquidus-zone between GaAs seed and feed as shown in Fig. 1.

By the interdiffusion in the liquidus-zone, spontaneous growth takes place at the interface between the seed crystal and liquidus-zone. According to our one-dimensional model, this spontaneous growth rate V is described by the following equation[11, 12] provided that diffusion-limited mass transport is realized in the liquidus-zone.

$$V = -\frac{D}{C_{L0} - C_{S0}} \left(\frac{\partial C}{\partial T} \right) \left(\frac{\partial T}{\partial z} \right)_{z=0} \tag{1}$$

where D is InAs-GaAs interdiffusion coefficient, C_{L0} and C_{S0} are solute concentrations in a liquid and in a solid at the freezing interface, respectively. $\partial C/\partial T$ is reciprocal of the slope of the liquidus and $\partial T/\partial z$ is temperature gradient.

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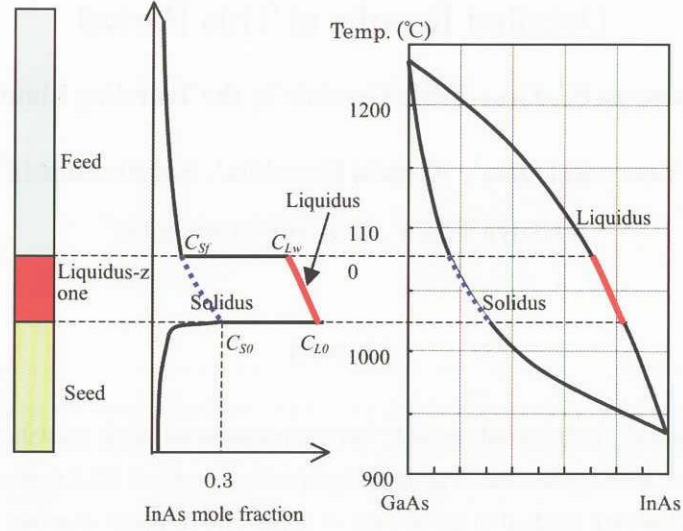
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Fig. 1 The relationship among the sample configuration, solute concentration profile in the TLZ method and the phase diagram of the InAs-GaAs system.

In the spontaneous growth, the interface shifts gradually to the hotter side. As a result, the concentration of InAs at the interface is decreased.

In the TLZ method, the sample device is translated toward the colder side in harmonizing with the spontaneous
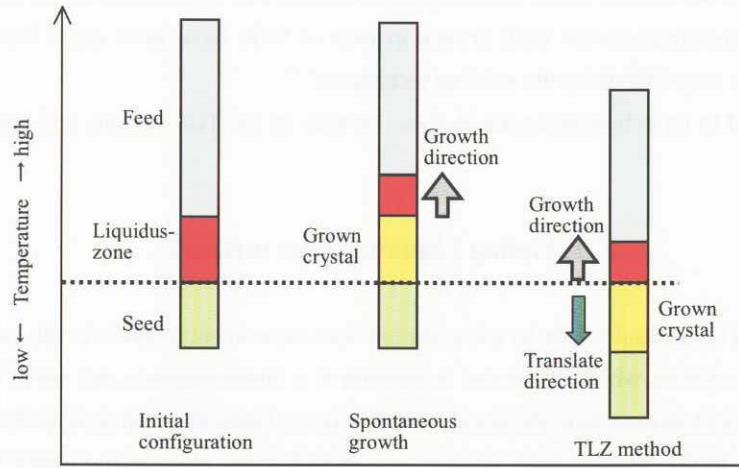

Fig. 2 Principle of realizing homogeneous concentration by the TLZ method.

growth rate, resulting in homogeneous concentration[13] (Fig. 2).

3. Procedure for growing homogenious Si$_{0.5}$Ge$_{0.5}$ crystals

The Si-Ge phase diagram is reported[14]. Therefore, we can determine C_{L0}, C_{S0} and $\partial C/\partial T$ easily from the diagram (Fig. 3). The respective value is 0.83 for C_{L0}, 0.50 for C_{S0} and 1.48×10^{-3}/K for $\partial C/\partial T$. Concerning $\partial T/\partial Z$, 10℃/cm which was used for the growth of InGaAs is applied because the growth of Si$_{0.5}$Ge$_{0.5}$ is carried out under
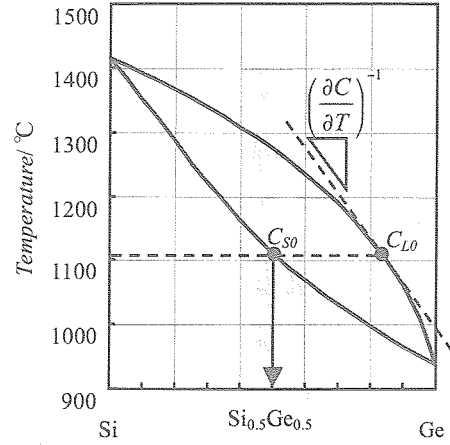
Fig. 3   Phase diagram of the SiGe system[14].

the same furnace conditions as those for the InGaAs growth.

However, it is difficult to determine a precise V from the one-dimensional model under the conditions in which the interdiffusion coefficient is unknown. Then we tried to determine the V for homogeneous composition by the following steps :

1)   With using the calculated interdiffusion coefficient $D=1.7\times10^{-4}cm^2/s$ by the first principle[15], $V=0.27mm/h$ was lead as a first approximation. Then the crystal growth test was carried out. For grown crystal, compositional variation is mesured by an electron probe micro-analyzer (EPMA).

Still the value of interdiffusion coefficient in this case was the average of several values of Si and Ge calculated at around the melting point.

2)   If germanium composition is decreased as the crystal growth proceeds, it means that sample translation rate is too slow. Then the sample translation is set faster in the following growth experiment. Conversely, if the germanium composition is increased, sample translation rate is set slower than the previous experiment.

Such regulations in translation rate are repeated until homogeneous composition is achieved, and the most proper rate is determined.

4. Experiments

① **Growth of SiGe crystal**

The setup of growth configuration is schematically given in Figure 4. As shown in the figure, a silicon seed of 2mm in diameter and 10mm in length, a germanium rod of 2mm in diameter and 20mm in length and a silicon feed of 2mm in diameter and 50 mm in length are loaded in a BN crucible sequentially, and are sealed in vacuum in a qualtz ampoule. The reason for using such slender seed and feed is to reduce the influence of thermal convection in a melt. On the outside of the ampoule, six thermocouples were placed at fixed intervals. One of them was placed at the position of the interface between the silicon seed and the germanium rod. The temperature of the interface was kept at 1098°C in order to obtain homogeneous composition of $Si_{0.5}Ge_{0.5}$. The sample translation was done in accordance with the procedures described in the section 3.
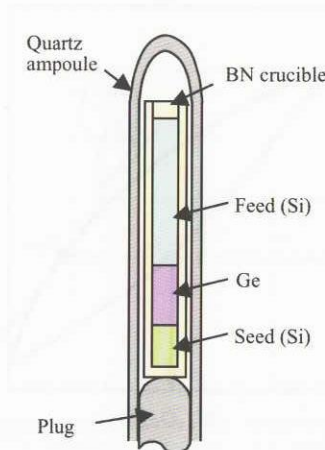
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Fig. 4   Schematic diagram of a sample device.

② **Analysis of composition**

After growth experiment, grown crystals were polished on the buff with diamond partticles of about $3\,\mu$m, and subsequently mirror polished with alumina particles of about $1\,\mu$m. Compositional analyses were carried out by EPMA at $100\,\mu$m intervals along the axis of growth direction.

③ **Characterization of grown crystals**

Crystallinity especially poly crystallized or monocrystallized structure, together with seeded state in the vicinity of the interface between the seed and the grown crystal were examined by the back reflection Laue camera. For grown crystals, their lattice parameters were also examined by the X-ray powder diffraction method.

5. Results and Discussion

① **Composition of grown SiGe crystals**

EPMA analyses made clear that germanium concentration decreased slightly with growth in the crystal grown at the sample translation rate of 0.27mm/h based on the first principle. On the contrary, the concentration increased gradually in the crystal obtained at 0.39mm/h. These results mean that the rate is slower in the former case and it is faster in the latter as compared with an appropriate rate. After fine regulations on the rate, it was found that an expected homogeneous crystal could be obtained at 0.29mm/h.

Figure 5 shows details of the experimental results mentioned above. The vertical axis corresponds to the variation of germanium concentration from the initial one in the growth direction. Germanium concentration of the crystal grown at 0.29mm/h is in the range of 0.50 ± 0.016 (Fig. 6). Therefore, the variation of composition is very small through the entire grown crystal.

Considering the proximity of this experimental result, that the proper translation rate was 0.29mm/h, to the calculated rate 0.27mm/h, the interdiffusion coefficient based on the first principle is approximately equal to its true value.
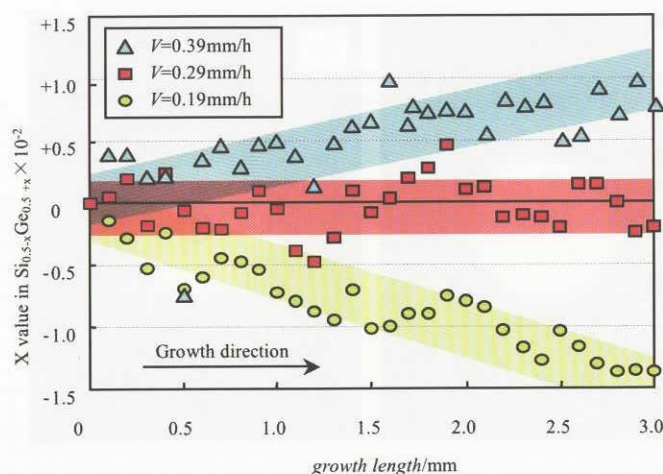
Fig. 5 Compositional profiles of SiGe crystals grown at various sample translating rates.
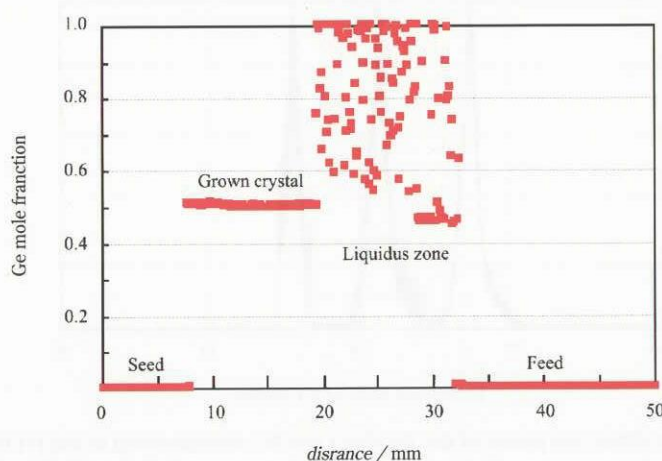

Fig. 6 Ge concentration profile in SiGe crystal grown by the TLZ method at the optimal sample translation rate.

② **Crystallinity of grown SiGe crystals**

The back reflection Laue patterns obtained in the seed and grown crystal regions are shown in Fig. 7. It becomes clear, from the figure, that these patterns are similar each other and excellent seeding is achieved in spite of the large compositional difference between the seed and the grown crystal. The reason why Laue spots of the grown crystal are unclear compared with those of seed is explained by relative inferiority of crystalline state. These results considerably differ from those of the InGaAs system, in which only poly crystals were grown from a GaAs seed. Further investigations on the seeding of the SiGe system will be needed in order to overcome difficulties in the seeding of the InGaAs system. Figure 8 shows diffraction peaks of Ge, $Si_{0.5}Ge_{0.5}$ and Si corresponding to the (111) reflection. The lattice constant of $Si_{0.5}Ge_{0.5}$ is 55.38nm, which agreed with the value determined by the Vegard's law, which is known as an experimental law for various alloys.
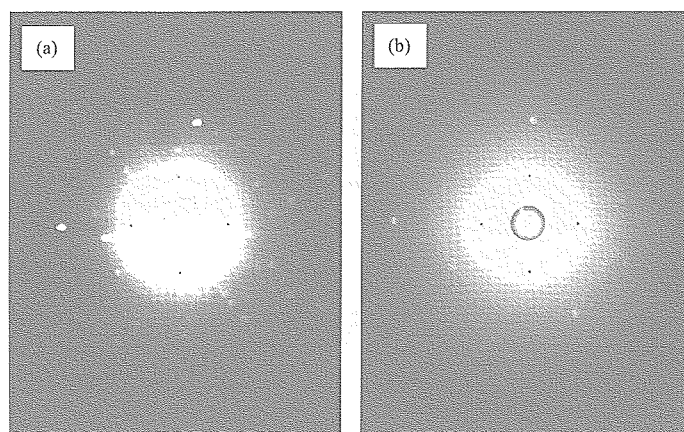
Fig.7   X-ray back Laue diffraction patterns of (a) Si-seed region and (b) grown crystal region.
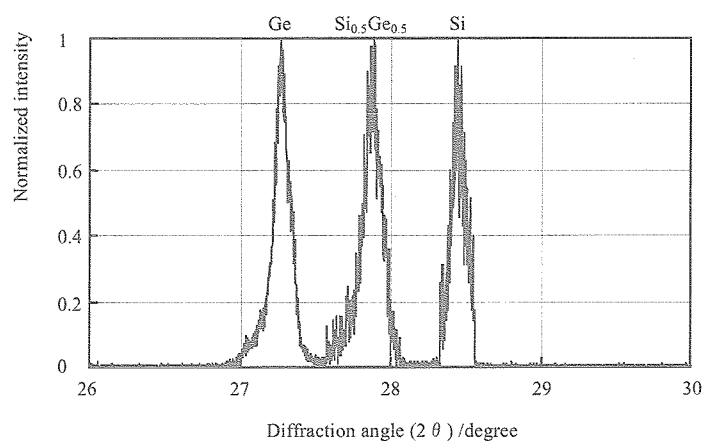

Fig. 8   X-ray powder diffraction peaks of Ge, $Si_{0.5}Ge_{0.5}$ and Si corresponding to the (111) reflection.

6. Conclusion

Growth of homogeneous $Si_{0.5}Ge_{0.5}$ single crystals by the TLZ method was tried and the following results were obtained.

1) Homogeneous $Si_{0.5}Ge_{0.5}$ bulk crystals of 2mm in diameter and 15mm in length were grown.

2) The compositional variation of the grown crystals was very small and ranged in 0.5 ± 0.016 in germanium mole fraction.

3) From diffraction patterns of back Laue camera, $Si_{0.5}Ge_{0.5}$ grown crystals took over the orientation of the Si seed crystal in spite of the large lattice mismatch.

4) From the results of X-ray powder diffraction, lattice constant of the $Si_{0.5}Ge_{0.5}$ grown crystal was 55.38nm.

5) Experimental results showed that the TLZ method was likely to be applicable to the Si-Ge system.

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