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Growth of $Si_{1-x}Ge_x$ bulk crystals with highly homogeneous composition for thermoelectric applications

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Abstract

Compositionally homogeneous $Si_{0.52}Ge_{0.48}$ bulk crystals were grown under a mild temperature gradient using a Si(seed)/ Ge/Si(feed) sandwich structure for thermoelectric (TE) applications. The furnace temperature was kept constant for 300 h for the growth of homogeneous $Si_{1-x}Ge_x$ bulk crystal with various temperature gradients. The temperature gradient of 0.4°C/mm resulted homogeneous $Si_{0.52}Ge_{0.48}$ bulk crystals of 22 mm length with Ge compositional fluctuation of about 0.0023/ mm. The compositions of the grown crystals were determined by means of Electron Probe Micro Analysis (EPMA). Electrical resistivity and Seeback coefficient of the prepared samples were measured using the in-house built measurement system. It was found that the compositional fluctuation of Ge was decreased as the temperature gradient of the furnace decreased. The prepared $Si_{0.52}Ge_{0.48}$ sample showed high Seeback coefficient compared to that of pure Si and Ge crystals.

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1. Introduction:

$Si_{1-x}Ge_x$ alloy semiconductor crystal is one of the most prominent materials for microelectronics, photovoltaic and various functional applications due to their lattice constant and band gap tuning based on the composition. In recent decades, there has been a rapidly increasing interest among the materials scientists concerning the growth of $Si_{1-x}Ge_x$ crystal especially due to its use as thermoelectric power generator at elevated temperature [1-3]. However, it is highly challenging to optimize the figure of merit (Z) by a suitable compromise between the thermal conductivity, k, Seebeck coefficient, α, and electrical conductivity, σ of the material. Moreover, the thermoelectric properties of the $Si_{1-x}Ge_x$ alloy are strongly dependent on the composition of the material rather than the crystalline nature of the alloy [3]. Therefore to enhance the thermoelectric performance of the material, it is necessary to grow the alloy crystal with homogeneous composition.

Several studies have been reported to grow $Si_{1-x}Ge_x$ bulk crystal with homogeneous composition such as continuous feeding Czochralski method [4,5], floating zone method [6], multi component zone melting [7-10] and travelling liquid zone method [11,12]. Despite of the enormous efforts made by the researchers using different methods, bulk growth of $Si_{1-x}Ge_x$ with homogeneous composition is still remaining as a highly challenging task. Nakajima et al [7] and their group [8] have been reported that the uniform $Si_{1-x}Ge_x$ bulk crystals were grown by balancing the pulling rate of the ampoule with the growth rate of the growing crystal, which was performed as a temperature control of the growth interface. However, this method is applicable only when the growth rate of the crystal is constant, but the actual growth rate is not constant for the entire growth period. Therefore, pulling down the ampoule at a constant rate would not be adequate to obtain $Si_{1-x}Ge_x$ crystal with homogeneous composition. Subsequently, the same group has developed an automatic feedback control (AFC) system for the position of the crystal-solution interface to keep the temperature at the interface constant during growth. Using such a sophisticated AFC system, they have grown a 23 mm long $Si_{0.22}Ge_{0.78}$ bulk crystal with homogeneous composition during 470 h growth period [9]. So, the variation of temperature at the growth interface results in the fluctuation of the composition of the grown crystal. Thus, one has to control the temperature at the growth interface, which is the key factor to obtain the homogeneous crystal. In the present investigation, without the aid of any sophisticated system like AFC, an attempt has been made to grow homogeneous $Si_{1-x}Ge_x$ alloy crystals by setting up the temperature gradient as mild as possible. Due to mild gradient, the crystal – solution interface temperature varies only very slightly along the growth direction which results homogeneous composition of the grown crystals. As a consequence, bulk crystals of $Si_{0.52}Ge_{0.48}$ up to 22 mm of length with very small Ge composition variations 0.0023/ mm) were grown under the temperature gradient of 0.4°C/mm. The compositions of the grown crystals were determined by means of Electron Probe Micro Analysis (EPMA). The thermoelectric properties of the grown samples were measured by using in-house built measurement system.

2. Experimental procedure:

2.1 Growth of $Si_{1-x}Ge_x$ bulk crystals with homogeneous compositions

For the growth of $Si_{1-x}Ge_x$ bulk crystals, a three-zone solid tubular furnace capable of operation at temperature up to 1200 °C was utilized. The temperature of each zone can be independently controlled. The quartz ampoule was filled with the polycrystalline Si as a seed, polycrystalline Ge as a solvent to form a SiGe growth solution and polycrystalline Si as a feeding material. A schematic representation of the sample configuration and cross-sectional view of the sample are shown in Fig. 1. All the three charge materials are cylindrically shaped with 23 mm of diameter. Prior to load the materials into the growth ampoule, the charge materials are chemically etched in a acid mixture of HF: HNO_3 with the ratio of 1:1 to remove surface oxides. Then the materials loaded quartz ampoule was evacuated to a pressure of approximately 5×10^{-3} Pa and sealed by a quartz sealing cap. Before the growth experiments, number of temperature profile measurements were taken to determine the best location for the growth ampoule within the outer quartz tube and to find suitable temperature for each zone of the furnace. The furnace was heated to the pre-determined temperature profile at a proper heating rate (300°C/ h) after placing the growth ampoule in an appropriate temperature gradient. Once the furnace reached the growth temperature, it was kept constant up to 300 h for dissolution and growth process. Thereafter, the furnace was gradually cool down to 800°C at a rate of -6°C/ h to reduce the thermal stress and cracks in the grown crystal. From the 800°C the furnace was allowed to natural cooling up to room temperature. The aim of the present investigation is to control the temperature variation at the growth interface by a mild temperature gradient. Thus, the SiGe growth experiments were performed for various temperature gradient ranges from 1 °C /mm to

0.4 °C /mm at the fixed growth temperature of 1124°C. The grown crystal was cut along the growth direction and polished to measure the compositional distribution.

2.2 Characterizations

The compositional distribution of the grown crystal was measured along growth and radial directions by EPMA analysis. The samples for Seebeck coefficient and electrical resistivity measurements were cut to the rectangular shape with the dimension of about 1 × 2 × 7 mm^3. The Seebeck coefficient was measured for the sample placed between the heating and non heating end. The electromotive force induced by the temperature difference of the hot (heating side) and cold (non heating side) end was detected by two thermocouples which are attached on the respective end of the sample using alumina paste. The Seebeck coefficient was calculated from the relation between electromotive force and temperature difference. The entire experiment was done under a vacuum environment ($\sim 10^{-1}$ Pa). The electrical resistivity of the sample was measured by the D.C. four probe technique. The resistance of the sample was measured as $R = V/I$, where I is the applied constant current (1 mA) and V is the voltage measured between the voltage probes. The electrical resistivity of the sample was obtained from the relation $\rho = R\times A/L$, where L is the distance between the voltage probes and A is the cross sectional area of the sample.

3. Results and Discussion:

During heating process, when the temperature around the growth ampoule reached the melting point of Ge, the polycrystalline Ge was started to melt. Once the Ge completely molten, it formed a growth solution by dissolving the feed and seed of Si while increasing the temperature to the growth temperature. Moreover, the solubility of the solvent mainly depends on the temperature at the dissolution interface. In the initial stage, dissolved solutes (in this case Si) at the seed interface were transported into the solution by solutal convection originating from the density difference between Si (2.33 g/cm^3) and Ge (5.323 g/cm^3). At the same time the dissolved solutes from the feed interface were transported towards seed interface mainly by diffusion originating from the concentration gradient [13]. When the time exceeds, solutal convection becomes week in the solution and the solute transport from the feed interface to seed interface is dominated by diffusion. As a result, the solution near the seed interface gets supersaturated which provides the necessary driving force to start the growth of SiGe at the growth interface.

The interface position shifts upwards as the SiGe crystal grows, which results in the variation of the growth temperature. Therefore, when a crystal grows under a steep temperature gradient, the Si composition is expected to increase gradually along the solidus line of Si-Ge phase diagram. To grow a SiGe crystal with homogeneous composition, the temperature at the growth interface must be controlled by adjusting the growth parameters. In the present growth experiment, in spite of a mild temperature gradient along the growth axis, the interface temperature variation along the growth direction was strongly suppressed which facilitated bulk growth of SiGe crystal with homogeneous compositions. Since the aim of the present experiment was to grow a compositionally homogeneous SiGe rather than a single crystal of SiGe for the application of thermoelectric devices, we have used poly crystalline Si seed and feed crystal for the growth of SiGe bulk crystals. Moreover, due to mild temperature gradient, the volume of constitutionally supercooled solution was large. As a result, the grown SiGe crystal was polycrystalline with homogeneous composition.

Fig. 2a shows EPMA data for compositional distribution of the $Si_{0.52}Ge_{0.48}$ bulk crystals grown under a temperature gradient of 0.4°C/ mm. The average Ge composition was 0.48 at the growth temperature of 1124 °C. It is seen from the figure 2a that the fluctuation of Ge composition is very small (0.0023/mm). The scattered points are probably due to the cracks in the crystals in addition with possible experimental errors. The scattered points are ignored for the calculation of composition gradient. The results reveal that the temperature variation at the growth interface is strongly suppressed by the low temperature gradient during the growth. The equilibrium temperature corresponds to the Ge composition as measured by EPMA was found to be same as the temperature existed near the growth interface position during the growth. It ascertains the optimum temperature distribution in the growth furnace. Fig. 2b shows the radial distribution of Ge composition measured at two different positions such as near the seed interface and 6 mm after the seed interface for the $Si_{0.52}Ge_{0.48}$ crystal. As can be seen from the figs. 2a and 2b, the compositional distribution of the gown crystal was homogeneous along the growth as well as radial direction.

The growth experiments were conducted by varying the vertical temperature gradient from 1°C/mm to 0.2°C/mm for the fixed growth temperature of 1124 °C at the growth interface. The Ge compositional fluctuation of the gown SiGe crystals is plotted as a function of vertical temperature gradient in Fig. 3. When the vertical temperature gradient was 1°C/mm, the compositional fluctuation of about 0.008/mm was observed in the grown crystals. While decreasing the temperature gradient to 0.4°C/mm, the compositional fluctuation was relatively decreased as 0.0023/mm in the grown SiGe bulk crystals. When the temperature gradient was decreased to 0.2°C/mm, growth was not started from the seed interface probably due to large volume of constitutionally supercooled melt. As can be seen from the Fig. 3, the Ge composition-fluctuation was decreased as the vertical temperature gradient of the furnace decreased. Moreover, the results reveal that 0.4°C/mm is likely to be a minimum critical temperature gradient for the compositionally homogeneous growth of SiGe bulk crystals from the Si Seed crystals.

Figure 4 shows the electrical resistivity variations of the grown crystal as a function of temperature. The resistivity of the polycrystalline Si and Ge were measured for reference. As can be seen from the Fig. 4, $Si_{0.52}Ge_{0.48}$ alloy shows gradual decrease of electrical resistivity with temperature. On the other hand, the polycrystalline Si and Ge show rapid decrease of resistivity with increasing the temperature. The electrical resistivity (ρ) is higher for Si and SiGe alloys compared to pure Ge, probably due to change in the intrinsic carrier concentrations which are determined by the band gap energy [14]. Figure 5 shows the Seebeck coefficient (α) of the grown crystals as a function of temperature. Moreover, the Seebeck coefficient of pure Si and Ge were measured for comparison and shown in Fig. 5. The magnitude of the Seebeck coefficient of the grown compositionally homogeneous polycrystalline $Si_{0.52}Ge_{0.48}$ alloy is higher than that of polycrystalline Si and Ge. Moreover the Seebeck coefficient of the alloy decreases gradually at elevated temperatures which may originate from the effect of thermal excitation of carriers across the band gap from the conduction band, as derived theoretically by Slack and Hussain [15].

4. Conclusion:

$Si_{1-x}Ge_x$ bulk crystals were grown under a mild temperature gradient. An attempt has been made to grow compositionally homogeneous crystals by reducing the interface temperature gradient. As a consequence, $Si_{0.52}Ge_{0.48}$ bulk crystal of about 23 mm in length was grown with the compositional fluctuation of 0.0023/mm. Moreover, the order of compositional homogeneity of the grown crystal was increased when the temperature gradient was decreased. Electrical resistivity and Seeback coefficient of the prepared samples were measured using the in-house built measurement system. The prepared $Si_{0.52}Ge_{0.48}$ sample showed high Seeback coefficient compared to that of poly crystalline Si and Ge.

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Figure caption:

Figure 1: Schematic representation of the sample configuration and cross-sectional view of the sample. The solid, dotted and dashed lines on the sample shows the compositional measurement area along growth and radial directions.

Figure 2a: Ge compositional distribution along the growth direction for the grown $Si_{0.52}Ge_{0.48}$ crystal.

Figure 2b: Radial distribution of Ge composition of the $Si_{0.52}Ge_{0.48}$ crystal (i) near the seed interface (ii) 6 mm from the seed interface

Figure 3: Rate of change of compositional fluctuation as a function of temperature gradient. It is seen that the compositional fluctuation is very small for the mild temperature gradient.

Figure 4: Electrical resistivity variations with temperature for the grown crystals

Figure 5: The Seebeck coefficient of the crystals plotted as a function of temperature.

Fig. 1

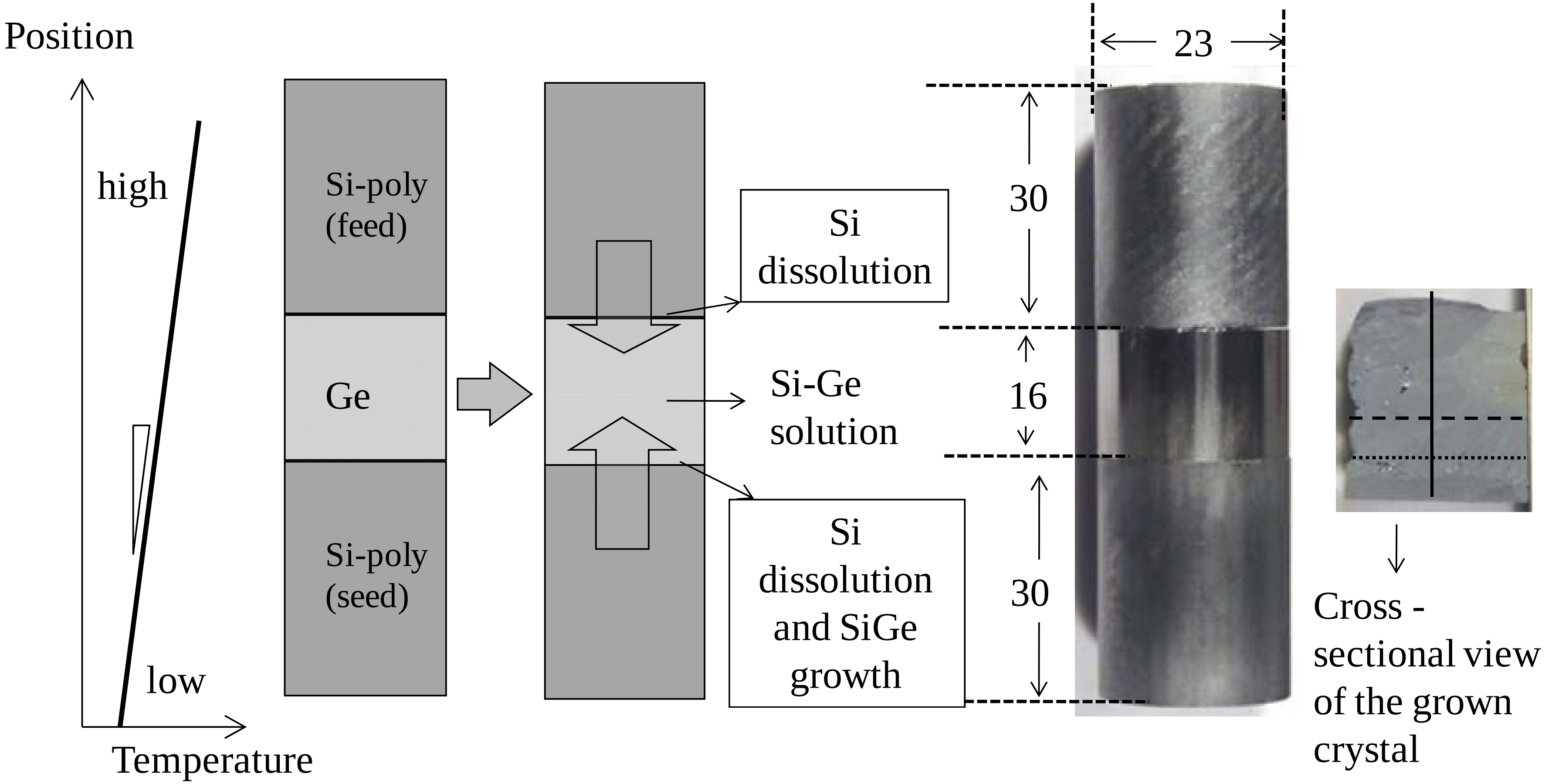

Position
high
low
Temperature
Si-poly
(feed)
Ge
Si-poly
(seed)
Si
dissolution
Si-Ge
solution
Si
dissolution
and SiGe
growth
23
30
16
30
Cross -
sectional view
of the grown
crystal

Fig. 2a

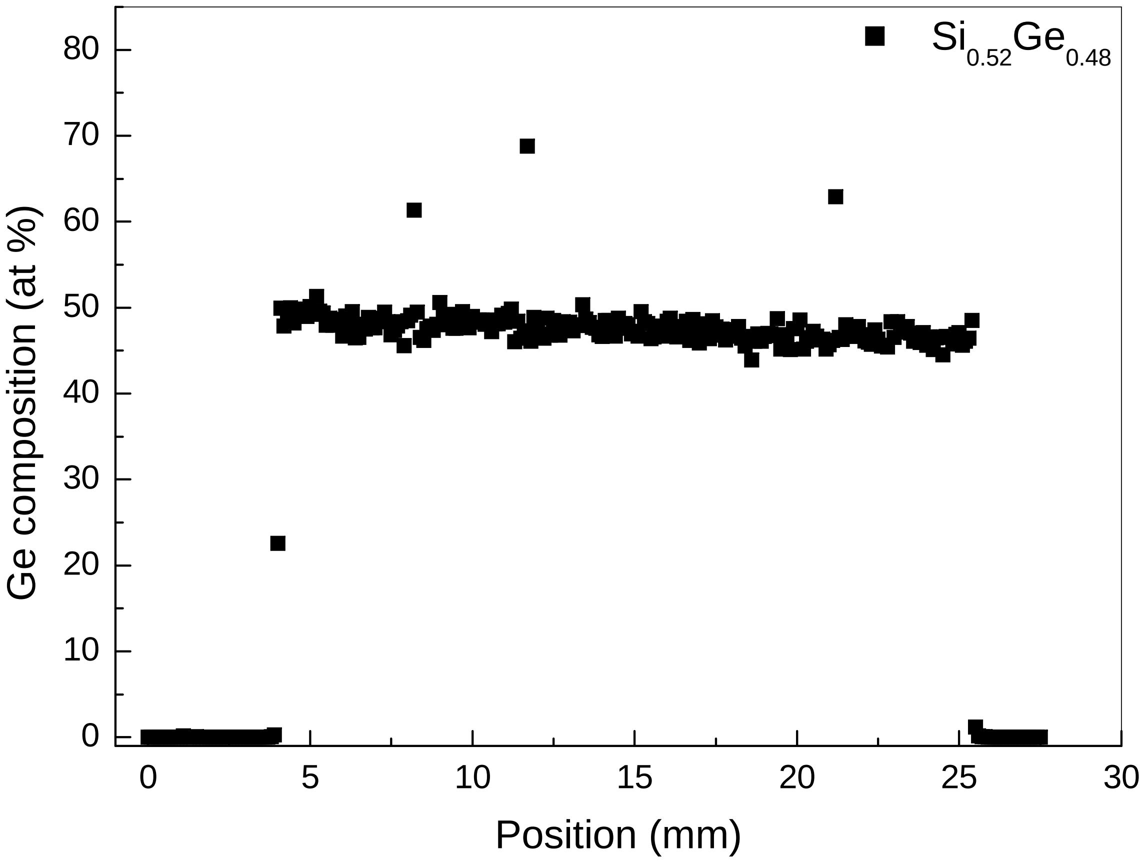

■ $Si_{0.52}Ge_{0.48}$
Ge composition (at %)
0
10
20
30
40
50
60
70
80
Position (mm)
0
5
10
15
20
25
30

Fig. 2b

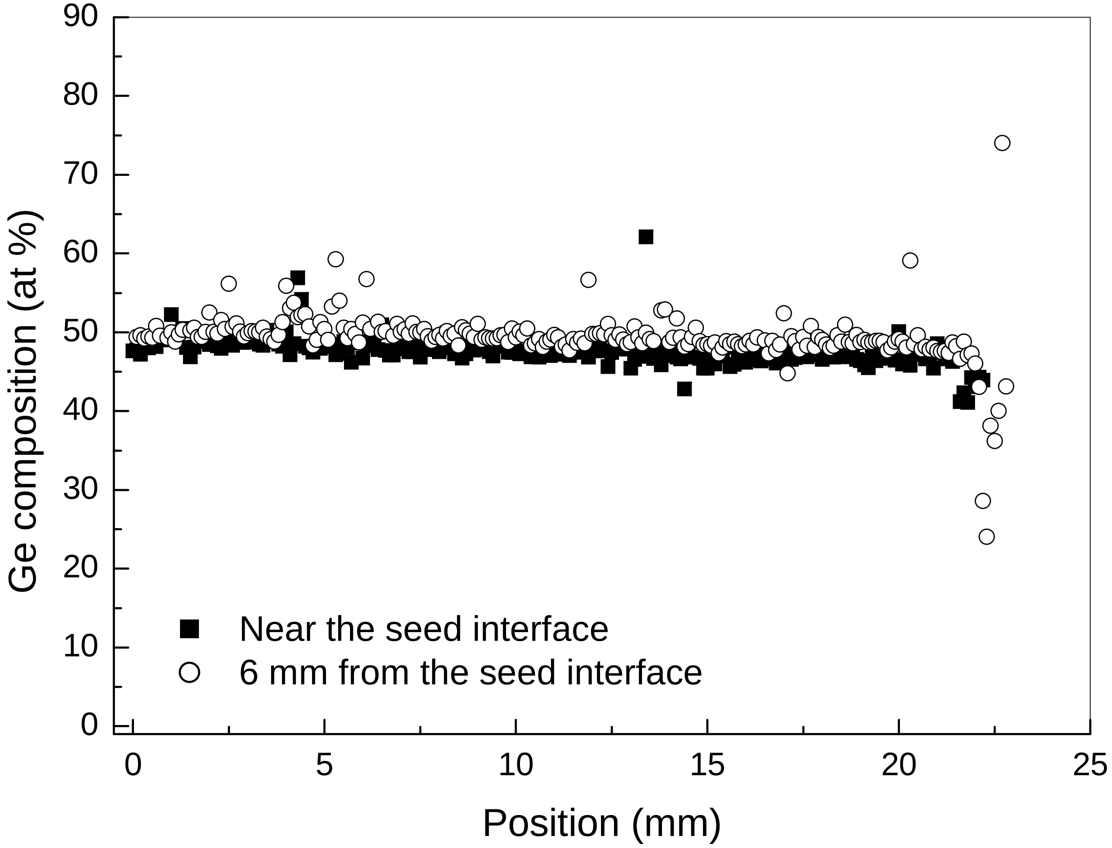
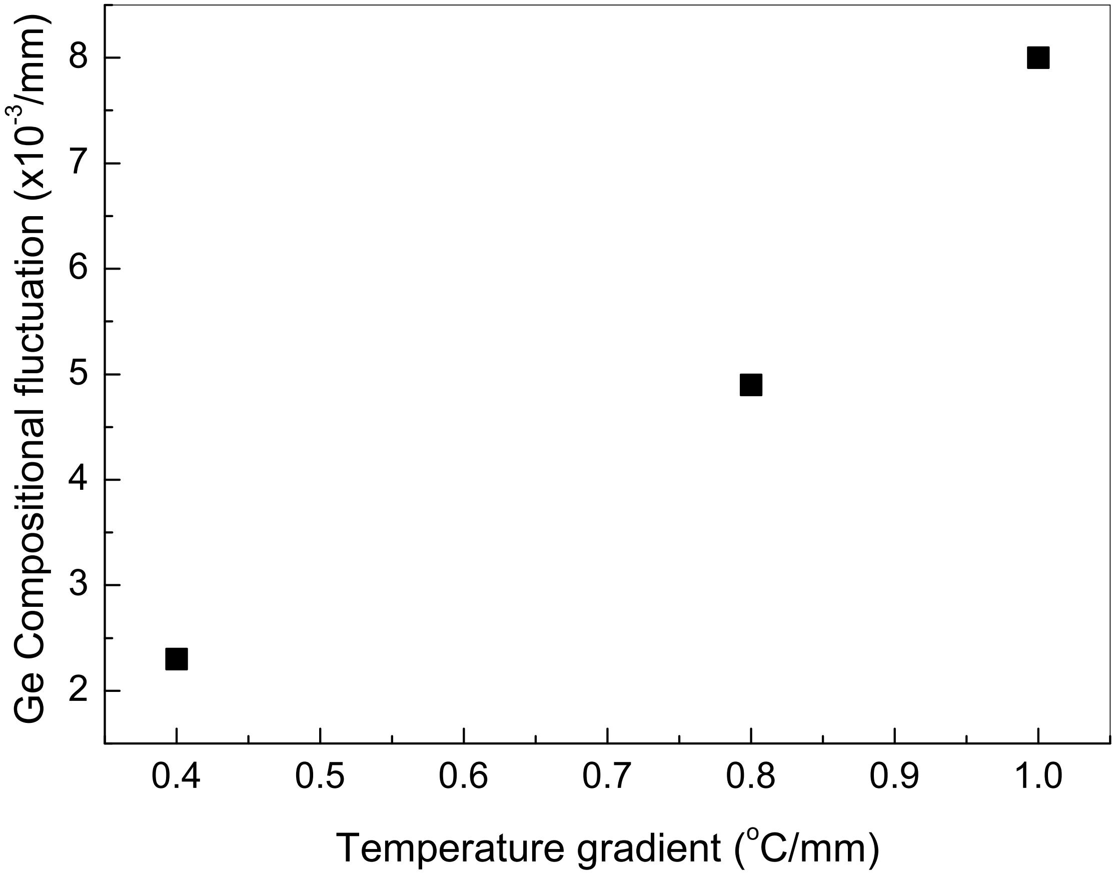
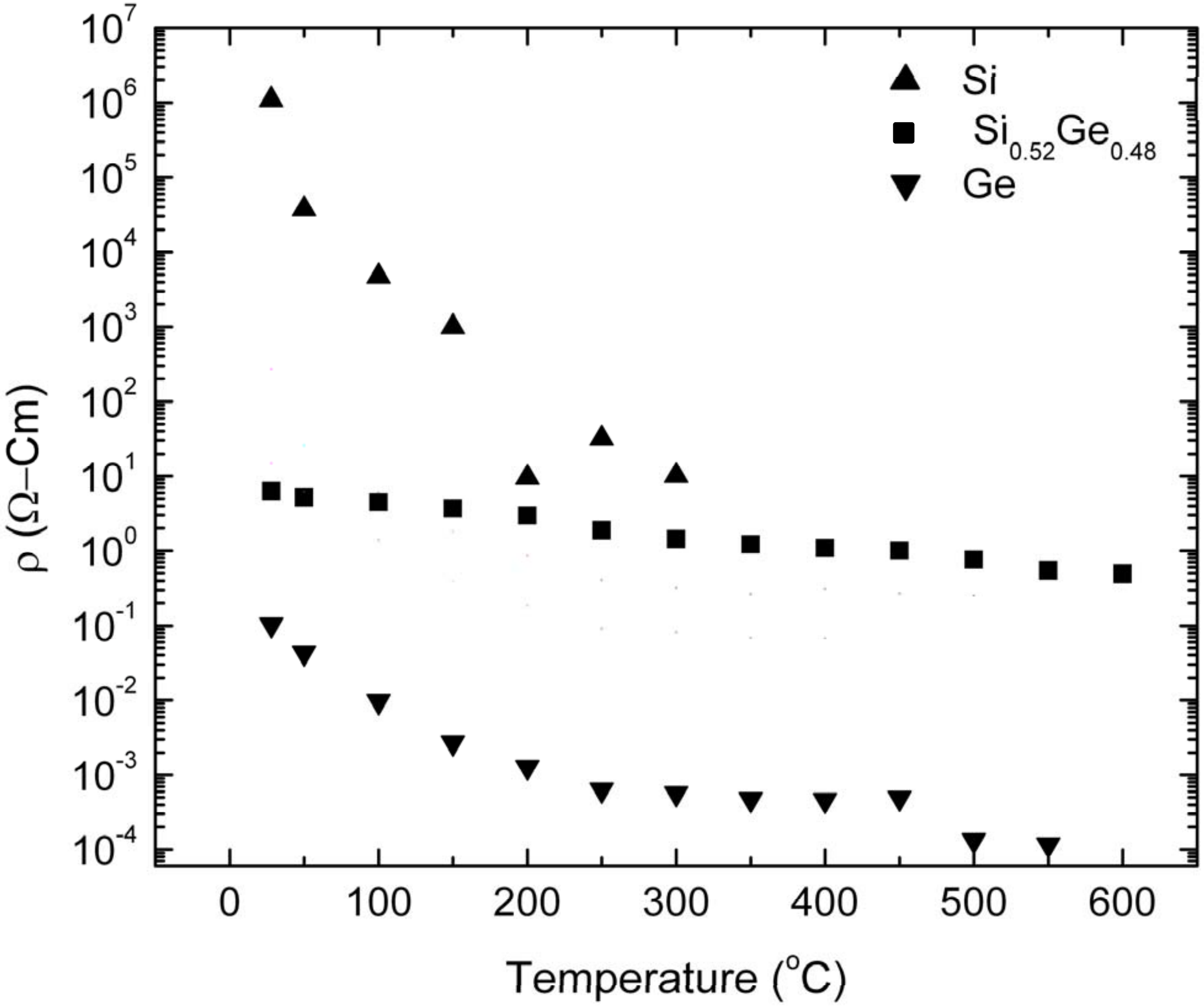

Ge composition (at %)
0
10
20
30
40
50
60
70
80
90
Position (mm)
0
5
10
15
20
25
■ Near the seed interface
○ 6 mm from the seed interface

Fig. 3



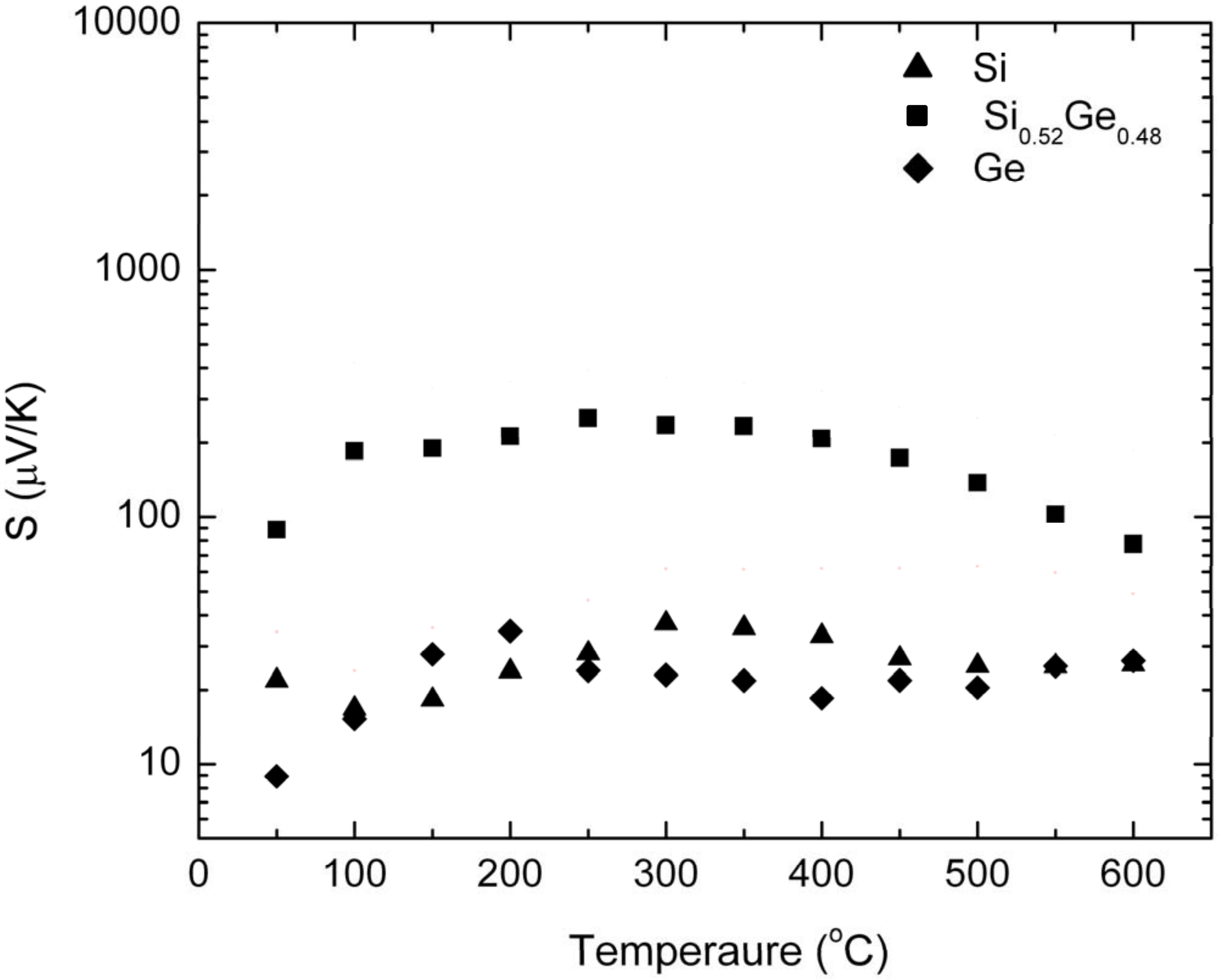
Ge Compositional fluctuation ($\times10^{-3}$/mm)
2
3
4
5
6
7
8
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Temperature gradient (^{o}C/mm)

Fig. 4



Si
Si0.52Ge0.48
Ge
ρ (Ω–Cm)
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-4
0
100
200
300
400
500
600
Temperature (°C)

Fig. 5



10000
1000
100
10
S (μV/K)
0
100
200
300
400
500
600
Temperaure (°C)
▲ Si
■ $Si_{0.52}Ge_{0.48}$
◆ Ge