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Temperature dependence of electron and hole mobilities in heavily impurity-doped SiGe single crystals

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Heavily impurity-doped single crystals of Si_xGe_{1-x} alloy with the composition $0.84<x<1$ and large-grained polycrystals with $x=0.80$ were grown by the Czochralski technique. The Hall-coefficient measurements of the electron and hole mobilities in the grown crystals were carried out in the temperature range of 300–1000 K and compared with those in undoped SiGe. The Hall mobilities of electrons and holes in SiGe with a carrier concentration of 10^{19}–10^{20} cm^{-3} both show a T^n, $n\sim1$, temperature dependence up to elevated temperatures. This indicates that the carrier transport process is mainly rate controlled by charged impurity scattering. In single-crystal SiGe free from grain-boundary effects, the hole mobility increases with decreasing Si content at least up to 0.84 and the electron mobility is greater than in Si and polycrystalline SiGe. These results suggest that scattering processes in alloy semiconductors are more complicated than previously thought. [DOI: 10.1063/1.2035890]

I. INTRODUCTION

Silicon-germanium alloys (Si_xGe_{1-x} or germanium-silicon $Ge_{1-x}Si_x$, where x is the mole fraction of Si) form a fully miscible solid solution with a diamond crystal structure. These alloys have attracted keen interest in view of their potential for band-gap and lattice-parameter engineering. SiGe thin films grown on Si substrates by various epitaxial techniques are being used for high-speed microelectronic devices. Also, bulk SiGe alloys have the potential for use as x-ray and neutron monochromators and solar cells, and might provide a lattice-matched substrate for SiGe epitaxial growth instead of Si. Highly conductive SiGe alloys are being employed in thermoelectric power generators operating at elevated temperatures up to about 1300 K. An electric power generation in SiGe alloys by conversion of a decay heat of Pt-238 has been employed in deep space probes such as Voyager, Galileo, and Cassini-Huygens. From the 1960s up to the present, extensive experimental and theoretical efforts have been aimed at enhancing the performance of SiGe alloys as thermoelectric devices.[1–3] For thermoelectric applications, however, in comparison with other basic factors such as the thermal conductivity and Seebeck coefficient, far less has been reported on the quantitative aspects of the carrier mobility, especially up to operating temperatures. One reason may be the general consensus that polycrystalline materials have a great cost advantage for these applications, although Slack and Hussain have suggested that a high-quality single-crystal SiGe might be a superior choice because grain-boundary scattering could be eliminated.[4] Moreover, single crystals do not suffer the adverse effects of dopants segregating at grain boundaries. What has most hampered the use of single crystals is the difficulty in preparing high-quality, unstrained bulk single crystals of SiGe alloys.

The present authors have attempted the Czochralski growth of large-sized Si_xGe_{1-x} bulk crystals in the whole composition range of $0<x<1$ and succeeded in growing high-quality single crystals of SiGe alloys of large sizes within the composition ranges of $0<x<0.15$ and $0.73<x<1$.[5] In order to further utilize and enhance the potential of SiGe, we are investigating various fundamental properties, as related to the alloying, of such high-quality crystals. For thermoelectric applications, the thermal conductivity, electrical conductivity, and Seebeck coefficient of high-quality single-crystal SiGe alloys were investigated in the temperature range of 300–1000 K.[6–8] The thermal conductivity was found to strongly depend on the alloy composition, explained by phonon scattering due to the lattice distortion at point defects in an alloy semiconductor. The experimentally observed Jonker relation, in which the Seebeck coefficient depends linearly on the electrical conductivity at 600 °C,[8] indicates the involvement of the charged impurity and alloy scattering mechanisms. Though fundamental carrier transport and scattering mechanisms governing thermoelectric properties can be deduced indirectly from such parameters, the direct determination of carrier mobilities is essential for both thermoelectric and microelectronic applications. Therefore, we herein report preliminary results on the carrier mobility of highly conductive SiGe single crystals at temperatures up to 1000 K.

II. EXPERIMENTAL PROCEDURE

Single crystals of Si_xGe_{1-x} alloy with the composition $0.84<x<1$ and large-grain-sized polycrystals with $x=0.80$ were grown by the Czochralski technique with a [001] Si seed crystal. Boron (B), gallium (Ga), or indium (In) was added as a p-type dopant and phosphorus (P) as an n-type dopant. The crystals were grown with a pulling rate in the

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TABLE I. Various characteristics of impurity-doped SiGe alloys at room temperature.

Si content x	Dopant (type)	Single/Poly	Hall mobility $cm^2/V\,s$ μ_e	Hall mobility $cm^2/V\,s$ μ_h	Carrier concentration $10^{19}\ cm^{-3}$
0.95	Ga(p)	Single		35	1.3
0.95	P(n)	Single	96		6.3
0.93	undoped ($p\rightarrow n$)[a]	Single		150[b]	0.0002[a]
0.93	B(p)	Single		32	2.3
0.93	P(n)	Single	163		0.43
0.90	undoped ($p\rightarrow n$)[a]	Single		266	0.000 006[a]
0.90	B(p)	Single		30	8.5
0.90	P(n)	Single	64		4.8
0.84	B(p)	Single		34	11
0.84	P(n)	Single	81		3.4
0.80	In(p)	Poly		24	3.4
0.80	P(n)	Poly	53		9.7

[a]The undoped specimens converted from p to n type at 200–300 °C.
[b]At 150 °C.

range of 2–5 mm/h in a flowing argon gas atmosphere. Details of Si_xGe_{1-x} alloy growth have been described elsewhere.[5,6,9] The alloy composition and homogeneity were determined by energy-dispersive x-ray spectroscopy. From the grown boules, square specimens with dimensions of $5\times5\times1\ mm^3$ were prepared for Hall-effect measurements. The Hall coefficient was measured by the Van der Pauw method from room temperature (RT) to 1000 K to determine the mobility and concentration of the electrons or holes.

III. RESULTS AND DISCUSSION

Table I summarizes the Si content, the Hall mobility (μ_e and μ_h), and carrier concentration at RT in the SiGe crystals investigated. Undoped $Si_{0.93}Ge_{0.07}$ and $Si_{0.9}Ge_{0.1}$ crystals were electrically p type at room temperature and became n type at temperatures in the range of 200–300 °C. The n- and p-type $Si_{0.8}Ge_{0.2}$ specimens were polycrystalline with a grain size of 50–100 μm.

Figure 1 shows the carrier concentrations as a function of temperature for the SiGe crystals. The carrier concentrations of the undoped $Si_{0.93}Ge_{0.07}$ and $Si_{0.9}Ge_{0.1}$ crystals increase rapidly with increasing temperature after their p to n conversion, while the concentrations of the heavily impurity-doped crystals are almost independent of temperature up to 800 K. Some specimens show a slight increase of carrier concentrations at temperatures above 800 K due to the increase of intrinsic carriers.

Figure 2 shows the variations of the electron and hole Hall mobilities for the SiGe crystals against temperature. Temperature variations of electron and hole mobilities in SiGe polycrystals reported previously are superimposed. The electron mobilities μ_e are somewhat higher than that in $Si_{0.7}Ge_{0.3}$ doped with P at $2.5\times10^{20}\ cm^{-3}$ by Vandersande,[10] reproduced in the paper by Slack and Hussain,[4] while the hole mobilities μ_h are the same or a little lower than those in low-density, hot-pressed $Si_{0.8}Ge_{0.2}$ doped with B at $2.4\times10^{19}\ cm^{-3}$ by Rowe[11] in the investigated temperature range. The μ_e in SiGe with the composition $0.8<x<1$ are higher than the μ_h in the whole temperature range investigated, the difference originating from the difference of the effective masses. At RT, in undoped SiGe crystals with the composition $0.8<x<1$, the electron mobility decreases from 1500 to $\sim500\ cm^2/V\,s$ and the hole mobility from 450 to 250 $cm^2/V\,s$ with increasing Ge content, and shows a somewhat flat bottom for Si content in the range of 0.5–0.8.[12] This can be explained in terms of the alloy scattering produced by the disorder fluctuations of the lattice potentials at the lattice sites as noted below. In Fig. 2, the μ_e and μ_h shown for the impurity-doped SiGe alloys are seen to be much lower than those in undoped specimens in the low-temperature region. μ_e and μ_h exhibit a gradual decrease with increasing temperature. Apparently, the temperature dependence of μ_e and μ_h in the SiGe crystals, especially in undoped crystals, becomes larger at higher temperatures, although this feature is not as pronounced in some crystals

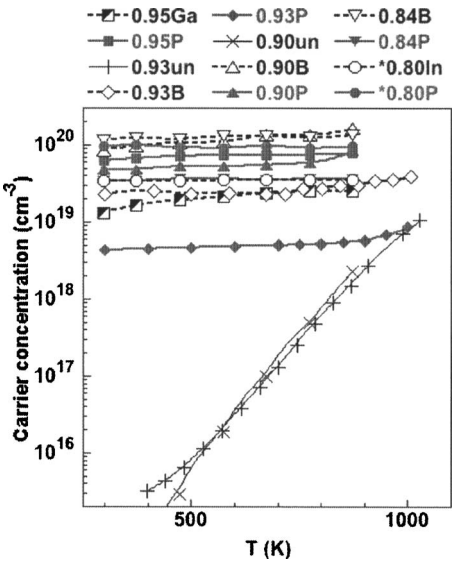

FIG. 1. Concentration of carriers in SiGe crystals plotted against temperature. The legend indicates the Si content and whether the species is doped or undoped. (*) means polycrystalline.

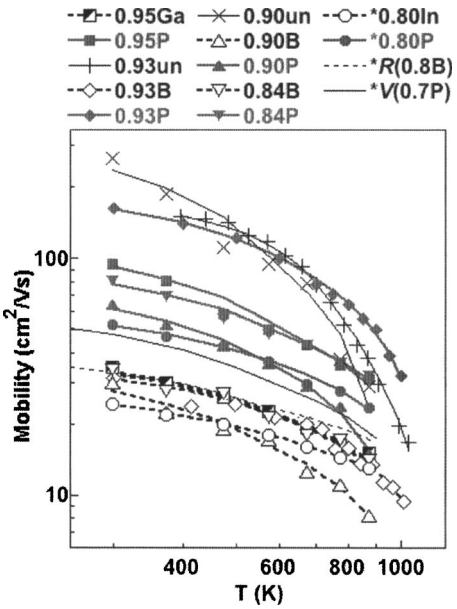

FIG. 2. Electron and hole Hall mobilities (μ_e and μ_h) in SiGe crystals plotted against temperature. The lines $^*V(0.7P)$ and $^*R(0.8B)$ indicate μ_e in P-doped $Si_{0.7}Ge_{0.3}$ with a concentration of 2.5×10^{20} cm^{-3} as reported by Vandersande (Ref. 10) and μ_h in hot-pressed $Si_{0.8}Ge_{0.2}$ doped with B with a concentration of 2.4×10^{19} cm^{-3} as reported by Rowe (Ref. 11). (*) means polycrystalline.

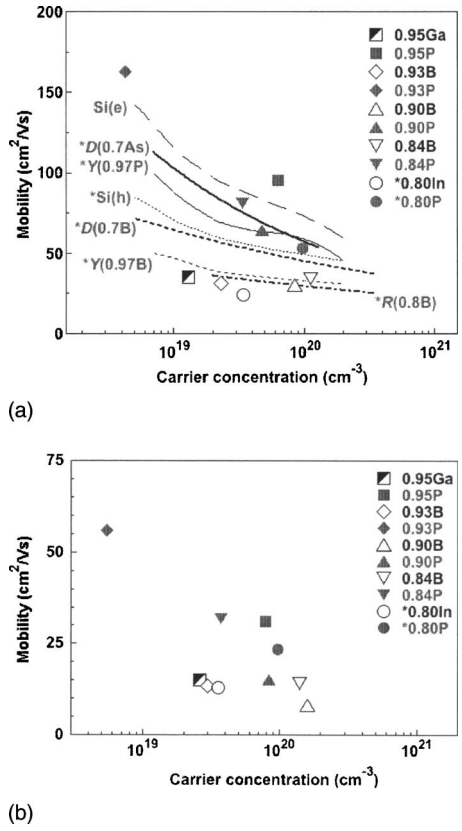

FIG. 3. Electron and hole Hall mobilities (μ_e and μ_h) in SiGe crystals plotted against the carrier concentration at (a) RT and (b) 600 °C. In (a), the lines $^*D(0.7As)$ and $^*D(0.7B)$ show the carrier-concentration dependences of electron and hole mobilities in As- and B-doped $Si_{0.7}Ge_{0.3}$ as reported by Dismukes *et al.* (Ref. 2). The line $^*R(0.8B)$ shows that of hole mobility in B-doped hot-pressed $Si_{0.8}Ge_{0.2}$ as reported by Rowe.[12] The lines $^*Y(0.97P)$ and $^*Y(0.97B)$ show electron and hole mobilities in P- and B-doped $Si_{0.97}Ge_{0.03}$ as reported by Yamashita and Sadatomi (Ref. 14). The lines Si(e) and Si(h) show those of electron and hole mobilities in Si as reported by Masetti *et al.* (Ref. 15). (*) means polycrystalline.

with a low hole mobility due to the heavy doping. The temperature at which the temperature dependence of μ_e and μ_h shifts from weak to large is higher in more heavily doped crystals.

The temperature dependence of the Hall mobilities (μ_e and μ_h) is described by the following equation:

$$\mu_e \text{ and } \mu_h \sim T^n, \tag{1}$$

where the exponent $n\approx1\pm0.1$, within experimental error, in the low-temperature region from RT to about 500 K, irrespective of the μ_e and μ_h values. At high temperatures, $n\approx3$ in the undoped $Si_{0.93}Ge_{0.07}$ and $Si_{0.9}Ge_{0.1}$ specimens and in n-type $Si_{0.93}Ge_{0.07}$. The obtained magnitude of n at low temperatures is comparable to that of n-type polycrystalline $Si_{0.7}Ge_{0.3}$ alloys reported by Vandersande,[10] and reproduced in the paper by Slack and Hussain.[4] Rowe reported that $n\approx0.8$ for hot-pressed B-doped $Si_{0.8}Ge_{0.2}$ alloys in the temperature range of 300–950 K.[11] In high-purity Si at room temperature $n=2.42$ and 2.20 are known for μ_e and μ_h, respectively.[13] Among the investigated SiGe crystals, $Si_{0.84}Ge_{0.16}$ and $Si_{0.8}Ge_{0.2}$ crystals show a weak variation of μ_e and μ_h with temperature up to the highest temperature. This may imply that carrier mobility is independent of temperature in the heavily impurity-doped SiGe alloys with such relatively high Ge contents.

Figures 3(a) and 3(b) show the relationship between the mobility and carrier concentration in the SiGe crystals at RT and 600 °C, respectively. In Fig. 3(a) the previous results in polycrystalline specimens of zone-level-grown $Si_{0.7}Ge_{0.3}$ reported by Dismukes *et al.*,[2] of hot-pressed $Si_{0.8}Ge_{0.2}$ by Rowe,[11] and of arc-melted $Si_{0.97}Ge_{0.03}$ by Yamashita and Sadatomi[14] are compared. The μ_e and μ_h versus carrier concentration relationships reported in Si by Masetti *et al.*[15] are also included. As seen in the figure, the measured μ_e and μ_h values decrease with increasing carrier concentration due to charged impurity scattering, as reported previously. The decrease of μ_e with increasing carrier concentration is much larger than that of μ_h. The values of μ_h in SiGe measured in the present work are close to those in polycrystalline SiGe reported by other groups[2,11,14] and are clearly lower than that in Si.[15] No systematic effect of different dopant species, such as Ga, In, or B, in p-type crystals can be detected explicitly. It is generally thought that μ_e is smaller in SiGe than in Si. In the present work, some SiGe samples were found to have similar values of μ_e as reported for polycrystalline SiGe by other groups, but it is seen that the single-crystalline $Si_{0.95}Ge_{0.05}$ and $Si_{0.93}Ge_{0.07}$ have greater values of μ_e than those observed for Si and polycrystalline SiGe.

At present, far less is known about the carrier mobility versus concentration relation at elevated temperatures compared with such relation at RT. In Fig. 3(b), the concentration-dependent features of μ_e and μ_h seem to be similar at RT and 600 °C, with μ_h having smaller magnitudes and weaker dependences than μ_e. Although the data in the present work are limited, a remarkable feature in single-crystalline alloys can be noted. The measured μ_h for a carrier

concentration of $\sim 10^{20}$ cm^{-3} seems to increase with decreasing Si content, i.e., in the order $Si_{0.95}Ge_{0.05}$, $Si_{0.9}Ge_{0.1}$, and $Si_{0.84}Ge_{0.16}$. Such enhancement effect was not observed for μ_e.

Several scattering mechanisms contribute to the carrier transport process in SiGe alloys: dominantly, carrier-phonon scattering, alloy disorder scattering, charged (ionic) impurity scattering, and so on. Intervalley phonon scattering due to L conduction-band transitions contributes to electron mobility when the electron concentration is higher than 10^{20} cm^{-3}.[16] Grain-boundary scattering can be excluded for single-crystal materials. Previously, based on the relation between the Seebeck coefficient and electrical conductivity, we reported that the carrier transport in heavily impurity-doped SiGe alloys is controlled by the alloy disorder and charged impurity scattering.[8] The present results reveal that μ_e and μ_h in heavily impurity-doped SiGe alloys have similar characteristic temperature dependence, especially at temperatures around RT. In the undoped SiGe, the electron mobility decreases rapidly with increasing temperature, which originates from carrier-phonon-scattering interaction, but not from impurity scattering. Thus, it can be assumed that the carrier transport is controlled by charged impurity scattering even at elevated temperatures in heavily impurity-doped SiGe and Si.

Due to the predominant contribution of impurity scattering, the effect of alloy scattering is not clearly seen in the heavily impurity-doped SiGe, although the electron and hole mobilities are generally lower in SiGe than in Si (with some exceptions). The hole mobility is observed to increase with decreasing Si content in the SiGe single crystals at carrier concentrations of $\sim 10^{20}$ cm^{-3}, though the alloying contribution is thought to increase, being proportional to an $x(1-x)$ relation.[17,18] The reason for this behavior is unclear at present. One possibility could be that potential fluctuations originating from the atomistic structure dominate the carrier transport. It has been reported that the phosphorus donor state leads to a rather broad infrared-absorption band in SiGe alloys even with low content less than around 0.05.[19] A similar behavior of the acceptor states is likely. Here, it can be noted that SiGe is an imperfect Pauling-type material,[20,21] that is, the local atomistic structure is accommodated by the changes of both the bond lengths and bond angles.

The μ_h in $Si_{0.95}Ge_{0.05}$ and $Si_{0.93}Ge_{0.07}$ single crystals is greater than in Si and polycrystalline SiGe. Slack and Hussain estimated that when the grains are smaller than 10 μm, grain boundaries affect the carrier transport.[4] However, there has also been a report that grain boundaries in SiGe have an electrically distorted region of about 10 μm in thickness,[22] which suggests a stronger influence of grain boundaries on carrier transport.

IV. SUMMARY

This paper presents preliminary results of carrier mobility in the heavily impurity-doped Si_xGe_{1-x} single crystals with the composition $0.84 < x < 1$ in the temperature range from RT to 1000 K. The Hall mobilities of electrons and holes in the SiGe with the carrier concentration of 10^{19}–10^{20} cm^{-3} both show the temperature dependence as T^n, $n \sim 1$, up to elevated temperatures, which suggests that carrier transport is controlled mainly by charged impurity scattering. Free from grain-boundary effects, the following two characteristics are detected in the SiGe single crystals: The hole mobility tends to increase with decreasing Si content to 0.84. The electron mobility in the Si-rich SiGe single crystals is greater than in Si and polycrystalline SiGe. These features, as well as recently acquired knowledge on the atomistic structure, suggest the necessity of reevaluating the role of scattering processes in SiGe alloys, including further examination in a wide temperature range.

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