Role of Nanoscale Precipitates for Enhancement of Thermoelectric Properties of Heavily P-Doped Si-Ge Alloys

Aikebaier Yusufu1,*, Ken Kurosaki1,*, Yoshinobu Miyazaki1, Manabu Ishimaru2, Atsuko Kosuga3, Yuji Ohishi1, Hiroaki Muta1 and Shinsuke Yamanaka1,4

1Graduate School of Engineering, Osaka University, Suita 565–0871, Japan
2Graduate School of Engineering, Kyushu Institute of Technology, Fukuoka 804–8550, Japan
3Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, Osaka 599–8570, Japan
4Research Institute of Nuclear Engineering, University of Fukui, Tsuruga 914–0055, Japan

Thermoelectric (TE) devices can save energy by generating electricity from waste heat. For industrial application of TE power generation, TE materials with high conversion efficiency and that are non-toxic and inexpensive are required. The nanostructured silicon-germanium (Si-Ge) alloy is one possible candidate for such TE materials. Nanostructuring is an effective way to improve the conversion efficiency of materials because it dramatically reduces the lattice thermal conductivity ($\kappa_{\text{lat}}$). Here, we experimentally demonstrate effective phonon blocking without carrier mobility deterioration in bulk Si-Ge alloys containing phosphorous-rich nanoscale precipitates connected coherently or semi-coherently with the matrix phase. When the Ge content was less than 5%, the nanoscale precipitates effectively scattered heat-carrying phonons, leading to a sufficient reduction in $\kappa_{\text{lat}}$. However, at higher Ge content compositions, phonon scattering by Ge substitution with Si was more predominant than phonon scattering by nanoscale precipitates for the reduction of $\kappa_{\text{lat}}$. As a result, significant enhancement of $zT$ was achieved at low Ge contents.

1. Introduction

Huge amounts of energy are exhausted as waste heat from the primary energies1 used in all fields, including industry, agriculture, and everyday life. Thermoelectric (TE) energy conversion could lead to significant energy savings by generating electricity from waste heat.2–4) The conversion efficiency of a TE energy conversion device depends on the properties of the TE material used and the temperature difference applied across the device. The effectiveness of a TE material is represented by the dimensionless figure of merit, $zT = (S^2\sigma T)/(\kappa_{\text{lat}} + \kappa_{\text{el}})$, where $S$, $\sigma$, $T$, $\kappa_{\text{lat}}$, and $\kappa_{\text{el}}$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and electronic and lattice components of the thermal conductivity ($\kappa$), respectively.5,6) $S$, $\sigma$, and $\kappa_{\text{lat}}$ depend on the carrier concentration of maximizing $S^2\sigma$, meaning that $zT$ can be effectively increased by decreasing $\kappa_{\text{lat}}$. At the present moment, the best bulk TE materials are bismuth telluride (Bi$_2$Te$_3$) and lead telluride (PbTe) materials, whose $zT$ values are around unity, corresponding to device efficiencies of several %. Although these conventional materials exhibit relatively high $zT$ values, they contain highly toxic and/or rare elements; thus, high-efficiency TE materials made from elements that are nontoxic, less expensive, and more Earth abundant need to be developed.

Because silicon (Si) is a nontoxic, cost effective, and naturally abundant semiconductor, it has many compelling advantages, which make it an ideal TE material. However, its only disadvantage for use as a TE material is that the bulk Si has a very high $\kappa_{\text{lat}}$ (>100 W m$^{-1}$ K$^{-1}$ at room temperature), leading to a maximum $zT$ value of 0.2.6) Therefore, many efforts have focused on reducing the $\kappa_{\text{lat}}$ of bulk Si. The $\kappa_{\text{lat}}$ of Si can be greatly decreased by forming a solid solution with germanium (Ge), and the best composition, Si$_{100-x}$Ge$_x$ ($x = 20–30$), shows the highest $zT$ value, of approximately 0.7–0.8.7–10) However, issues such as the still low $zT$ and the high cost of Ge have limited the industrial applications of these materials. Recently, it has been experimentally proven that nanostructuring also reduces the $\kappa_{\text{lat}}$ and hence greatly improves the $zT$ of various materials,11–15) including bulk Si and Si-Ge alloys.6,16–19) Indeed, very recently, our group has demonstrated that nanostructured bulk n-type Si heavily doped with phosphorous (P) containing a small amount of Ge, less than 3 at.%, shows a maximum $zT$ of 0.6 at 1050 K,20) three times higher than that of non-nanostructured, i.e., traditional, bulk Si. In our nanostructured bulk Si, P-rich nanoscale precipitates can be naturally formed by optimizing the heat treatment conditions of the samples. Because the nanoscale precipitates connect coherently or semi-coherently with the Si matrix, they effectively scatter heat-carrying phonons without significantly influencing the electron transport properties, leading to high $zT$ values.20) It is thought that further improvement of $zT$ is possible if the Ge content could be optimized. As described before, the optimized Ge content in Si-Ge alloys is 20–30 at.%. Thus, in the present study, we attempted to synthesize heavily P-doped Si-Ge alloys containing naturally formed nanoscale precipitates and investigated the role of the precipitates in the enhancement of the TE properties of Si-Ge alloys. The nominal sample compositions studied here were Si$_{100-x}$Ge$_x$P$_y$ ($x = 0, 1, 3, 5, 10$, and $20$).

2. Experiment

The starting materials, Si chunks (11N), Ge shots (5N), and P chunks (4N), were weighed and mixed to the desired compositions and melted by arc melting in an Ar atmosphere. The
ingots produced by arc melting were then crushed into micropowders, which were placed in a graphite die for spark plasma sintering (SPS) at 1353 K for 3 min under an axial pressure of 100 MPa in an Ar atmosphere. The bulk samples produced by SPS were characterized using powder X-ray diffraction (XRD; Rigaku RINT2000) with Cu-Kα radiation at room temperature. The microstructure and chemical composition of the samples were studied using scanning electron microscopy (SEM; Hitachi S-2600H) and energy-dispersive X-ray spectroscopy (EDX; Horiba EX-200). The density (d) of each bulk sample was calculated based on its measured weight and dimensions.

Nanoscale structures were characterized by transmission electron microscopy (TEM). For each TEM observation, each thin specimen was prepared by crushing the bulk sample into powders and then collecting the powders on a perforated amorphous carbon film supported by a copper grid. TEM was performed at an accelerating voltage of 200 kV in bright-field mode (Hitachi HF2000), with an ultrahigh-sensitivity energy dispersive X-ray spectroscopy instrument.

σ and S were measured simultaneously in a He atmosphere at 323–1073 K (Ulvac ZEM-3). The Hall coefficient (R_H) was measured (Toyo Resitest8300) at room temperature by the van der Pauw method in vacuum under an applied magnetic field of 0.5 T. The Hall carrier concentration (n_H) and Hall mobility (μ_H) were calculated from R_H by assuming a single-band model and a Hall factor of 1; i.e., n_H = 1/(eR_H) and μ_H = σR_H, where e is the elementary electric charge. k was evaluated from the thermal diffusivity (α), heat capacity (C_p), and d by k = αC_pd. k was measured at 323–1073 K by the laser flash diffusivity method (Netzsch LFA-457).

C_p data for pure Si were used to calculate the k for samples of Si_{1-x}Ge_{0.547}P_{0.453} (x = 0, 1, and 3) and the C_p data estimated from those of pure Si and pure Ge based on the Kopf–Neumann rule were used to calculate the k for samples of Si_{1-x}Ge_{0.547}P_{0.453} (x = 5, 10, and 20).

3. Results and Discussion

The phase state of the samples was characterized by powder XRD. As shown in Fig. 1(a), all samples were confirmed to have a single phase with a diamond structure (Fd-3m space group) without any noticeable secondary phases within the detection limit of our XRD equipment. In addition, all the XRD peaks were shifted to lower angles with increasing x in Si_{100-x}Ge_x, implying that the unit cell volume slightly expands. Figure 1(b) shows the lattice parameters (a) calculated from the XRD patterns as a function of Ge content. The a values are also summarized in Table 1. The a should increase with increasing Ge content because the atomic radius of Ge is larger than that of Si. In contrast, a should decrease by P-doping because the atomic radius of P is smaller than those of Si and Ge. The results in Fig. 1(b) show that the a values of the samples were slightly lower than the line for pure Si-Ge alloys predicted by Vegard’s law.

Table 1 summarizes the properties of the samples. All the samples exhibited very high d, corresponding to above 98% of the theoretical value. All samples exhibited high Hall μ_H, on the order of 10^{20} cm^{-3}. The n_H showed a tendency to decrease with increasing Ge content. This behavior can be explained by the solubility limit of P in Si-Ge alloys, which decreases with increasing Ge content. All samples exhibited similar values for the (μ_H, at approximately 50 cm^2V^{-1}s^{-1}). Figure 2(a) and 2(b) show the temperature dependences of S and σ, respectively. As expected, all samples exhibited negative S over the entire temperature range, indicating n-type conduction, meaning that electron doping by adding P into Si-Ge alloys was performed successfully. As the temperature increased, the absolute S increased, while the σ decreased, showing the typical behavior of degenerate semiconductors. Above approximately 900 K, the temperature dependency of absolute S and σ tended to change, likely related to the increased carrier concentration caused by the increased solubility limit of P for Si-Ge alloys at high temperatures. Fig. 2(c) shows the theoretical Pisarenko line, calculated using eqs. (1), (2), and (3). Under the single-parabolic-band model, S can be expressed as follows:

\[ S(T) = S(300) \left(1 - \frac{T}{T_p}\right)^{3/2} \]

where \( T_p \) is the temperature at which the Seebeck coefficient is zero.

Table 1 Lattice parameter a, density d, Hall carrier concentration n_H (300 K), Hall mobility μ_H (300 K), Seebeck coefficient S (300 K), electrical conductivity σ (300 K), lattice thermal conductivity κ_θ (300 K), and maximum zT_max (1070 K) of samples with nominal compositions of Si_{100-x}Ge_{x}P_{x} (x = 0, 1, 3, 5, 10, and 20).

<table>
<thead>
<tr>
<th>Composition</th>
<th>a (nm)</th>
<th>d (g/cm^3)</th>
<th>n_H (10^{20} cm^{-3})</th>
<th>μ_H (cm^2V^{-1}s^{-1})</th>
<th>S (μVK^{-1})</th>
<th>σ (10^{2} S m^{-1})</th>
<th>κ_θ (Wm^{-1}K^{-1})</th>
<th>zT_max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si_{100}P_{3}</td>
<td>0.54237</td>
<td>2.30</td>
<td>98</td>
<td>3.84</td>
<td>43</td>
<td>-77</td>
<td>2.52</td>
<td>25</td>
</tr>
<tr>
<td>Si_{90}Ge_{10}P_{3}</td>
<td>0.54243</td>
<td>2.35</td>
<td>98</td>
<td>3.54</td>
<td>45</td>
<td>-75</td>
<td>2.31</td>
<td>12</td>
</tr>
<tr>
<td>Si_{80}Ge_{20}P_{3}</td>
<td>0.54343</td>
<td>2.40</td>
<td>98</td>
<td>2.09</td>
<td>53</td>
<td>-87</td>
<td>2.12</td>
<td>9</td>
</tr>
<tr>
<td>Si_{70}Ge_{30}P_{3}</td>
<td>0.54377</td>
<td>2.44</td>
<td>98</td>
<td>2.10</td>
<td>53</td>
<td>-85</td>
<td>2.13</td>
<td>8</td>
</tr>
<tr>
<td>Si_{60}Ge_{40}P_{3}</td>
<td>0.54466</td>
<td>2.60</td>
<td>97</td>
<td>2.18</td>
<td>49</td>
<td>-90</td>
<td>1.89</td>
<td>5</td>
</tr>
<tr>
<td>Si_{50}Ge_{50}P_{3}</td>
<td>0.54738</td>
<td>3.00</td>
<td>98</td>
<td>1.93</td>
<td>48</td>
<td>-100</td>
<td>1.39</td>
<td>4</td>
</tr>
</tbody>
</table>
where $\eta, m^*, k_B, h, F(\eta)$, and $\lambda$ are the reduced Fermi level ($=E_F/k_BT$, where $E_F$ is the Fermi level), carrier effective mass ($=1.08m_0$), Planck constant, Fermi integral, and scattering parameter, respectively. $\lambda$ is a parameter associated with the energy dependence of the charge-carrier mean free path, where we obtained $\lambda=0.65$ by fitting the literature data for bulk Si and Si-Ge alloys. This value is reasonable because it has been reported that values of $\lambda$ between 0 and 1 are a good fit to experimental $S$ values for Si-Ge alloys. As can be seen in Fig. 2(c), our data existed on the theoretical Pisarenko line. The $\mu_H$ versus $n_H$ relationship for the samples at 300 K is shown in Fig. 2(d), together with the calculated curves using the literature data for single crystalline Si [20] and polycrystalline n-type Si$_{100}$Ge$_{30}$ [31]. The $\mu_H$ data for samples of Si$_{100}$P$_3$ and Si$_{90}$Ge$_{10}$P$_3$ existed on the Si curve, while with increasing Ge content, e.g., for samples of Si$_{100}$Ge$_{30}$P$_3$ ($x=3, 5, 10,$ and 20), the $\mu_H$ data existed on the Si$_{90}$Ge$_{10}$P$_3$ curve. This behavior implies that the point-defect scattering caused by Ge substitution with Si is dominant for carrier scattering and is the primary factor that determines the magnitude of $\mu_H$. The results shown in Fig. 2(c) and 2(d) indicate that the electrical transport properties of our samples are similar to those reported for traditional bulk Si and Si-Ge alloys.

The microstructures of the samples were characterized by SEM and TEM. From the SEM analysis, it was confirmed that all samples were dense, with no remarkable cracks and pores, and that their grain sizes ranged from several micrometers to a few dozen micrometers (for example, see Supporting Information of Ref. 20). Quantitative analysis using EDX spectroscopy equipped with the SEM revealed that Ge was uniformly distributed in the samples and that the samples' contents were nearly the same as their starting compositions. However, we could not obtain accurate P contents because it was within the error range of the EDX.

Figure 3 shows the TEM images of samples with compositions of Si$_{100}$Ge$_x$P$_3$ ($x=0, 1, 3$, and 20). In the present study, the TEM observation was carried out for the sample of Si$_{98}$Ge$_{2}$P$_3$. The TEM images for the samples of Si$_{100}$Ge$_x$P$_3$ ($x=0, 1, and 3$) were obtained in our previous study. In all the TEM images, nanoscale precipitates with various sizes under a few dozen nanometers can be clearly observed. As described in our previous paper, two types of nanoscale precipitates naturally form in the grains of the polycrystalline Si-Ge alloys. One is plate-like P-rich precipitates with sizes of a few dozen nanometers, and the other is spherical precipitates with diameters of several nanometers. As reported in Ref. 20, we have confirmed that the plate-like and spherical precipitates had P-rich compositions by using the TEM/EDX analysis and a lattice image modelling. Similar nanostructures have been observed in a Cu-Al alloy, in which Cu-rich nanoinclusions naturally precipitate in the Al matrix and harden the alloys, called precipitation hardening or age hardening. In Si-Ge alloys, it has been confirmed that plate-like and spherical precipitates are semi-coherently and coherently connected with the matrix phase, respectively. As shown in Fig. 3, there are no remarkable differences in the sizes and distribution of the precipitates among the samples with different Ge contents. The temperature dependences of $\kappa$ of the samples are plotted in Fig. 4(a). As the Ge content increased, the $\kappa$ decreased throughout the whole measured temperature range. $\kappa_{\text{el}}$ was obtained by subtracting $\kappa_{\text{ph}}$ from $\kappa$. The electronic part was

$$S = \frac{k_B}{e} \left[ \eta - \frac{(2 + \lambda)F(1+\lambda)(\eta)}{(1 + \lambda)F(\eta)} \right],$$

$$n_H = 4\pi \left( \frac{2m^*k_BT}{h^2} \right)^{3/2} F_{1/2}(\eta),$$

$$F(\eta) = \int_0^\infty \frac{x'dx'}{1 + \exp(x - \eta)}.$$
calculated by the Wiedemann–Franz relationship, i.e., $\kappa_{el} = \frac{L\sigma T}{\rho T}$, where $L$ is the Lorenz number and can be calculated with the following expression:

$$L = -\frac{k_B^2}{e^2} \frac{(1 + \lambda)(3 + 4\lambda)F_3(\eta)F_{2+1}(\eta) - (2 + \lambda)^2 F_{1+1}(\eta)^2}{(1 + \lambda)^2 F_{1}(\eta)^2},$$

(4)

where $\eta$ values were obtained by fitting the temperature dependence of experimental $S$ using eq. (1). As shown in Fig. 4(b), the calculated $L$ values for all samples are lower than that of the metallic limit of $2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$, and decrease with increasing temperature throughout the entire temperature range. As can be seen in Fig. 4(c), the $\kappa_{lat}$ decreased with increasing Ge content throughout the whole temperature range because of the enhancement of point-defect scattering of phonons caused by Ge substitution of Si. Additionally, the $\kappa_{lat}$ of the samples were rather flat, slightly decreased with temperature, and did not follow the $T^{-1}$ or $T^{-0.5}$ relationship. This temperature dependence of $\kappa_{lat}$ implies that complex phonon scatterings caused by not only Umklapp scattering but also other scatterings occur in this system. Figure 4(d) shows a comparison of experimental and theoretically calculated $\kappa_{lat}$ at 330 K for the samples. The theoretical lines were calculated using a Born–von Karman dispersion model including frequency-dependent expressions for grain-boundary scattering.31) In this model, $\kappa_{lat}$ can be expressed as:

$$\kappa_{lat} = \frac{1}{3} \int C \cdot \nu^2 \cdot \tau_c \cdot d\omega,$$

(5)

where $C$, $\nu$, $\tau_c$, and $\omega$ are the specific heat capacity, group velocity, relaxation time, and frequency, respectively. When calculating $\kappa_{lat}$, we considered four types of phonon scattering: Umklapp scattering (phonon-phonon scattering), phonon-impurity scattering (in other words, point-defect scattering), phonon-grain boundary scattering, and phonon-electron scattering. Thus, we estimated $\tau_c$ as follows:

$$\tau_c^{-1} = \tau_{umkl}^{-1} + \tau_{imp}^{-1} + \tau_{bdy}^{-1} + \tau_{ep}^{-1},$$

(6)

where $\tau_{umkl}$, $\tau_{imp}$, $\tau_{bdy}$, and $\tau_{ep}$ are the relaxation times determined by Umklapp scattering, phonon-impurity scattering, phonon-grain boundary scattering, and phonon-electron scattering, respectively. All of the scattering parameters have been summarized in Table S1 in the Supporting Information of Ref. 20. In Fig. 4(d), for nondoped Si$_{100-x}$Ge$_x$, the experimental data obtained from the literature32) are consistent with

![Fig. 4](image-url)
the theoretical line. The theoretical line was calculated when Umklapp scattering, phonon-impurity scattering (in this case, impurity means Ge), and phonon-grain boundary scattering were taken into account. Conversely, the theoretical line, calculated when Umklapp scattering, phonon-impurity scattering (in this case, impurity means both Ge and P), grain-boundary scattering, and phonon-electron scattering were taken into account, was clearly higher than those of the experimental \( \kappa_{\text{lat}} \) for \( \text{Si}_{100-x}\text{Ge}_x\text{P}_3 \), especially for low Ge content. However, the calculated values decreased with increasing Ge content, and almost completely agreed with the experimental values, when the Ge content was up to 20%. This means that additional phonon scatterings should be taken into account to understand the experimental \( \kappa_{\text{lat}} \) of \( \text{Si}_{100-x}\text{Ge}_x\text{P}_3 \), especially at low Ge content. This additional scattering may be caused by the nanoscale precipitates observed in the TEM images (Fig. 3).

It has been demonstrated in various materials that nanostructuring reduces \( \kappa_{\text{lat}} \), but in many cases, the nanostructuring also deteriorates carrier mobility to some degree.\(^{33-35}\) However, as shown in Fig. 2(d), the Si-Ge alloys containing nanoscale precipitates prepared in the present study exhibit values of carrier mobility similar to those of traditional Si-Ge alloys that do not contain nanostructures. This means that, in this system, the nanoscale precipitates scatter phonons effectively but scatter electrons very little. Indeed, in our samples, it has been confirmed that the nanoscale precipitates coherently or semi-coherently connect with the matrix phase,\(^{20}\) and these types of matched interfaces have little influence on the electron transport properties.\(^{36-38}\) As can be confirmed in Fig. 4(d), the contributions of this additional scattering decrease with increasing Ge content in Si-Ge alloys. Thus, when the Ge content is low, the additional phonon scattering by nanoscale precipitates is predominant and effectively reduces the \( \kappa_{\text{lat}} \). However, when the Ge content increases and reaches approximately 20%, the point-defect scattering caused by substitution of Ge for Si becomes more predominant in the determination of \( \kappa_{\text{lat}} \) than the additional phonon scattering caused by the nanoscale precipitates.

Figure 4(e) shows the temperature dependence of \( zT \) of the samples with nominal compositions of \( \text{Si}_{100-x}\text{Ge}_x\text{P}_3 \) (\( x = 0, 1, 3, 5, 10, \) and 20). The \( zT \) of the samples increased with both temperature and Ge content. As a result, the maximum \( zT \) of 0.8 was obtained for the sample with \( x = 20 \) at 1073 K. Figure 4(f) shows the relationship between the maximum \( zT \) value and Ge content of the samples. In this figure, the \( zT \) values of non-nanostructured Si-Ge alloys calculated theoretically are shown for comparison. In the low Ge content region, the maximum \( zT \) values of nanostructured Si-Ge alloys are approximately three times larger than that of non-nanostructured Si, while, in the high Ge content region (e.g., the sample with \( x = 20 \)), the nanostructured Si-Ge alloys exhibit almost the same \( zT \) values as that of non-nanostructured Si-Ge alloys. This means that as the Ge content increases, the contribution of nanoscale precipitates is reduced but the point-defect scattering caused by substitution of Ge for Si becomes predominant in the determination of \( \kappa_{\text{lat}} \). Therefore, it can be concluded that the nanoscale precipitates enhance the \( zT \) of Si-Ge alloys only when the Ge content is low.

4. Conclusions

Polycrystalline samples of \( \text{Si}_{100-x}\text{Ge}_x\text{P}_3 \) (\( x = 0, 1, 3, 5, 10, \) and 20) with nominal compositions were prepared, and the TE properties were examined. The following conclusions were obtained. In heavily P-doped Si-Ge alloys, two types of P-rich nanoscale precipitates, semi-coherent plate-like precipitates with sizes of a few dozen nanometers and coherent spherical precipitates with diameters of several nanometers, naturally form. There are no remarkable differences in the sizes and distribution of the precipitates among the samples with different Ge contents. The nanoscale precipitates have negligible influences on the electron transport properties, while effectively scattering heat-carrying phonons, leading to a significant reduction in \( \kappa_{\text{lat}} \) while maintaining a high power factor. With low Ge content, phonon scattering caused by the nanoscale precipitates is the predominant factor in the reduction of \( \kappa_{\text{lat}} \), while at high Ge content, point defect phonon scattering caused by Ge substitution for Si is predominant. As a result, the nanoscale precipitates effectively enhance the \( zT \) of Si-Ge alloys when the Ge content is small, i.e., less than 5%.

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