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Bottom-up nanostructured bulk silicon: A practical high-efficiency thermoelectric material

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The effectiveness of Thermoelectric (TE) materials is quantified by the dimensionless figure of merit \( zT \). An ideal way to enhance \( zT \) is by scattering phonons without scattering electrons. Here we show that, using a simple bottom-up method, we can prepare bulk nanostructured Si that exhibits exceptionally high \( zT \) of 0.6 at 1050 K, at least three times higher than that of optimized bulk Si. The nanoscale precipitates in this material connected coherently or semi-coherently with the Si matrix, effectively scattering heat-carrying phonons without significantly influencing the material’s electron transport properties, leading to the high \( zT \).

Introduction

The energy demands of economic and social development are continually rising. However, over 60% of primary energy is exhausted as waste heat, 1 necessitating efficient re-use of waste heat. Thermoelectrics (TEs) can generate electricity from a temperature difference according to the Seebeck effect; inversely, applying a current electrical generator a temperature difference according to the Peltier effect. These effects can be respectively used to generate power from waste heat and for solid-state refrigeration. 2-4 However, current TE devices have low efficiency, limiting their applications in power generation to niche areas such as in NASA spacecraft.5

Extensive industrial applications, such as generating power from exhaust heat in automobiles, have not been achieved.

The efficiency of a TE 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 \( zT = (S^2/\sigma)T/(\kappa_\text{eh}+\kappa_\text{lat}) \), where \( S \), \( \sigma \), \( T \), \( \kappa_\text{eh} \), and \( \kappa_\text{lat} \) are the Seebeck coefficient, electrical conductivity, absolute temperature, and electronic and lattice components of the thermal conductivity, respectively. 6 \( S \), \( \sigma \), and \( \kappa_\text{lat} \) depend on the carrier density of the material, meaning that \( zT \) can be effectively increased by decreasing \( \kappa_\text{lat} \). The best materials currently used in TE devices are PbTe-based materials for power generation at high temperatures5 and Bi2Te3-based materials for refrigeration near room temperature.7 The \( zT \) values of these conventional materials are \( \approx 1 \), corresponding to device efficiencies of several percent. Along with their inadequate efficiency, these conventional materials contain highly toxic and/or rare elements such as Bi, Te, and Pb. Thus, many desire to develop high-efficiency TE materials made from elements that are less expensive, more Earth-abundant, and more environmentally friendly.

Si is a non-toxic, inexpensive, and naturally abundant element. Although bulk Si exhibits good electrical properties (i.e., high \( S/\sigma \)), its \( \kappa_\text{lat} \) is high (\( \approx 100 \text{ Wm}^{-1}\text{K}^{-1} \)), leading to a \( zT \) of \( \approx 0.01 \) at room temperature.8 If its \( \kappa_\text{lat} \) could be lowered while maintaining high \( S/\sigma \), Si could be an ideal TE material. These changes can be realized in Si by nanostructuring.7, 9-16

Bulk nanostructured TE materials are typically made in one of two ways: forming a bulk by fabricating and consolidating fine nanocrystals (top-down process) or forming a bulk by precipitating nanoscale particles (bottom-up process). These top-down structures are commonly prepared by using ball milling (BM) followed by hot pressing (HP) or spark plasma sintering (SPS). Top-down methods are effective and have been used to prepare various conventional TE materials, including Bi2Sb2Te3 and Si–Ge14, 15 alloys. Top-down p-type Bi2Sb2Te3 bulk nanocrystals have exhibited a maximum \( zT \) of 1.4,7 compared to a peak \( zT \) of \( \approx 1 \) for conventional bulk materials. However, top-down methods have some drawbacks: undesirable impurities may be incorporated during BM, nanocrystals may grow too much during HP/SPS, and oxidation may be difficult to avoid during BM and/or HP/SPS.

Bottom-up materials are usually prepared by solidifying a melt under appropriate cooling conditions. Bottom-up SrTe–PbTe materials, in which nanoscale SrTe is naturally precipitated in the PbTe matrix, have exhibited record-high \( zT \) of \( \approx 2.2 \).16 However, bottom-up methods have been realized almost in lead chalcogenides such as PbS17, PbSe,18 and PbTe,17, 19

Because Si nanopowders oxidize easily, it is difficult to apply the BM-HP/SPS method to create bulk nanostructured Si. The Si–Ge nanocrystals reported so far have been prepared under carefully controlled atmospheres, such as in an Ar-filled globe box.14, 15 In the
present study, we successfully prepared bulk nanostructured Si using an easy, reliable, bottom-up method, by arc melting super-heavily P-doped Si, crushing it into micropowder, and then performing SPS in desirable conditions. Two kinds of nanoscale precipitates naturally formed in the grains of the polycrystalline Si matrix: semi-coherent plate-like P-rich precipitates with sizes of a few dozen nanometres, and coherent spherical precipitates with diameters of several nanometres Fig. 1a. These nanoscale precipitates effectively scattered the heat-carrying phonons without significantly influencing the material’s electron transport properties, greatly decreasing its thermal conductivity and leading to a $zT$ of 0.6 at 1050 K, at least three times higher than that of optimized bulk Si Fig. 1b.

In the Si–P phase diagram (see Fig. S1 in the Supplementary Information), the solubility of P in Si depends much on temperature: the solubility limit is $\approx 2.4$ at.\% at 1453 K and almost zero at room temperature. This phase diagram suggests that a P-rich phase will form in the grains of the polycrystalline Si matrix: semi-coherent plate-like P-rich precipitates with sizes ranging from a few dozen nanometres and coherent spherical precipitates with sizes of several nanometres. (b) Temperature dependence of $zT$ in nanostructured bulk Si with an uncertainty of 12%.

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Results and Discussion

As shown in Fig. 2 the powder XRD patterns of the present samples exhibited very sharp peaks corresponding to Si with no impurity peaks, revealing them to be single-phase materials. Table 1 summarizes the lattice parameters ($a$) calculated from these XRD patterns. The $a$ of Si100P1 and Si100P3 were smaller than that of pure Si ($a = 0.5431$ nm,$^{21}$ and Si100P3 exhibited a slightly smaller $a$ than Si100P1. Adding Ge (i.e., Si99Ge1P3 and Si97Ge3P3) increased $a$ with increasing Ge content. We attribute these results to the atomic radius of P (0.110 nm)$^{22}$ being slightly smaller than that of Si (0.117 nm)$^{22}$ and because substituting Ge for Si increased the $a$ of Si. SEM images (see Fig. S2 in the Supplementary Information) revealed that all samples were dense with no remarkable cracks and pores and that their grain sizes ranged from several micrometres to a few dozen micrometres. Quantitative EDX analyses revealed that Ge was uniformly distributed in the samples and that their 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 EDX. Table 1 summarizes the bulk densities of the samples, revealing that the sample densities were high enough ($\approx 98\%$ of theoretical density) for TE characterization.

Table 1 lists the $n_H$ and $\mu_H$ of the samples, calculated from measured room-temperature $R_H$. All samples exhibited very high $m_H$, on the order of $10^{20}$ cm$^{-3}$. For Si100P1 and Si100P3, $m_H$ increased with increasing P content because P-doping supplied electrons to Si. For Si99Ge1P3, Si97Ge3P3, and Si97Ge3P3, the $m_H$ decreased with increasing Ge content, despite their having the same P content as their starting compositions.

<table>
<thead>
<tr>
<th>$a$ (nm)</th>
<th>$d$ (g cm$^{-3}$)</th>
<th>%TD</th>
<th>$n_H$ ($10^{20}$ cm$^{-3}$)</th>
<th>$\mu_H$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$S$ (\mu V K$^{-1}$)</th>
<th>$\sigma$ (10$^4$ S m$^{-1}$)</th>
<th>$\kappa_{\text{lat}}$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$zT_{\text{max}}$</th>
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<tr>
<td>Si100P1</td>
<td>0.54238</td>
<td>2.30</td>
<td>98</td>
<td>1.82</td>
<td>56</td>
<td>-77</td>
<td>1.85</td>
<td>42</td>
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<tr>
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<td>98</td>
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<td>2.09</td>
<td>53</td>
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<td>2.12</td>
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</table>

Fig. 1 (a) Micro- and nanoscale schematics of nanostructured bulk Si prepared in the present study. The polycrystalline bulk Si, whose grain size ranged from several micrometres to a few dozen micrometres, contained two kinds of naturally formed nanoscale precipitates: semi-coherent plate-like P-rich precipitates and coherent spherical precipitates with sizes of several nanometres. (b) Temperature dependence of $zT$ in nanostructured bulk Si with an uncertainty of 12%.
compositions. This behaviour was caused by pure Si having higher P-solubility than Si–Ge alloys; the solubility limit of P is 2.4 at.% at 1453 K for pure Si\(^{20}\) and 1.8 at.% at 1050 K for a Si\(_{97}\)Ge\(_{3}\)P\(_{3}\) alloy.\(^{23}\) We also confirmed that samples with larger \(n_0\) had smaller \(\mu_0\).

Fig. 3 (a) and (b) show how \(S\) and \(\sigma\) depended on temperature, respectively. Fig. 3(a) reveals that all samples exhibited negative \(S\), indicating the samples were \(n\)-type and the majority carriers were electrons. As the temperature increased, the absolute value of \(S\) increased while \(\sigma\) decreased, typical behaviour of degenerate semiconductors. These tendencies agree well with previous data for Si-based TE materials.\(^{14, 15}\) Above \(\approx 900\) K, the temperature dependency of the absolute values of \(S\) and \(\sigma\) tended to change, likely related to the increased carrier concentration caused by the increased solubility limit of P for Si at high temperatures. We could not confirm a clear relationship between \(S\) and \(\sigma\) with the samples, we calculated and analysed the \(\kappa_0\) of nanostructured bulk Si. In (c), lines calculated from the Born–von Karman dispersion model are shown; lines 1, 2, 3, 4, and 5 represent the calculated results for non-doped single crystal Si, heavily-doped polycrystalline Si (3\(\times\)10\(^{20}\) cm\(^{-3}\)), highly-doped polycrystalline Si containing 1 at.% Ge (3\(\times\)10\(^{20}\) cm\(^{-3}\)), grain size: 5 \(\mu\)m, and heavily-doped polycrystalline Si containing 3 at.% Ge (3\(\times\)10\(^{20}\) cm\(^{-3}\)), grain size: 5 \(\mu\)m, respectively.

\[ S = \frac{k}{e} \left[ \frac{n - (2 + \lambda) F_H(\eta)}{(1 + \lambda) F(\eta)} \right], \]  
\[ \eta = \frac{m^* k T}{h^2}, \]  
\[ F(\eta) = \int_0^\eta \frac{dx}{1 + \exp(x - \eta)}, \]  

where \(\eta, m^*, k, h, F(\eta), \) and \(\lambda\) are the reduced Fermi level (= \(E_F/k_b T\), where \(E_F\) is the Fermi level), carrier effective mass (= 1.08m\(_0\)/\(\gamma\) where \(m_0\) is the free electron mass), Boltzmann constant, Planck constant, Fermi integral, and scattering parameter, respectively. \(\lambda\) is a parameter that explains the energy dependence of the charge-carrier mean free path; \(\lambda = 0, 1, \) and \(2\) correspond to both acoustic phonon scattering and alloy disorder scattering, optical phonon scattering, and ionized impurity scattering, respectively.\(^{30}\) In the present study, we obtained \(\lambda = 0.65\) by fitting the literature data.\(^{15, 24, 25}\) A reasonable result because it has been reported that \(\lambda = 0−1\) gives a good fit to experimental \(S\) values for Si–Ge alloys.\(^{30}\) Examining Fig. 3 (c), we confirm that our data exist on the theoretical Pisarenko line. Also, Fig. 3 (d) shows that the relationship between \(n_0\) and \(\mu_0\) for our data almost matched those from the literature data of Si-based TE materials.\(^{15, 25-27}\) These results indicate that the electrical transport properties of our samples are similar to those of traditional Si-based bulk TE materials.
phonon scattering, and phonon-electron scattering. Each scattering parameter can be written as summarized in Table S1.

In this model, we considered four kinds of phonon scattering: Umklapp scattering, phonon-impurity scattering, grain-boundary phonon scattering, and phonon-electron scattering. The theoretical lines for non-doped (line 1) and heavily-doped (line 2) single crystal Si agree well with previous experimental data.14, 15 Comparing lines 1 and 2, we confirm that P doping of Si reduced \( \kappa_{\text{lat}} \) by influencing both phonon-impurity and phonon-electron scattering. Comparing lines 2 and 3, we confirm that polycrystalline Si with a grain size of 5 \( \mu \)m had slightly lower \( \kappa_{\text{lat}} \) than that of single crystal Si because of grain-boundary phonon scattering. Comparing lines 3, 4, and 5, we confirm that substituting Ge for Si significantly reduced \( \kappa_{\text{lat}} \) by increasing phonon-impurity scattering, even at low Ge content of 1–3 at.%. As described previously, the grain sizes of our samples ranged from several micrometres to a few dozen micrometres (see Fig. S2 in the Supplementary Information) and exhibited \( n_{\text{P}} \) values around \( 3 \times 10^{20} \) cm\(^{-3}\) (see Table 1). Thus, the experimentally determined \( \kappa_{\text{lat}} \) of Si\(_{100}\)P\(_3\), Si\(_{99}\)Ge\(_1\)P\(_3\), and Si\(_{97}\)Ge\(_3\)P\(_3\) should agree with the theoretically calculated lines of 3, 4, and 5, respectively. However, as shown in Fig. 3(f), the experimental \( \kappa_{\text{lat}} \) were significantly lower than those of the theoretical lines. To understand this difference, we carefully observed the microstructures of the samples by using TEM.

Fig. 4 shows the TEM microstructure of a bulk Si\(_{99}\)Ge\(_1\)P\(_3\) sample. The grain size in this sample was much larger than the image dimensions, so these images were mainly used to identify defects within a single grain. A bright-field (BF) image at low magnification (Fig. 4(a)) shows a high density of precipitates dispersed in a matrix as well as dark contrast around the precipitates, caused by strain. Because the precipitate density and size varied widely in each grain, quantitative analysis is difficult. We found similar precipitates in Si\(_{100}\)P\(_3\), Si\(_{99}\)P\(_3\), and Si\(_{97}\)Ge\(_3\)P\(_3\) (see Fig. S4 in the Supplementary Information). In these samples, the form and density of the precipitates appeared to be the same. However, the samples with less P had obviously smaller precipitate density.

The higher-magnification BF image in Fig. 4(b) shows two types of precipitates, both in morphology and size. One is a plate-like precipitate with a diameter of 15–100 nm. As indicated by arrow A, this type of precipitate exhibited high contrast, likely caused by misfit strain. As shown by arrow B, we also observed areas of lesser contrast. These differing contrasts were likely caused by the differences in the directions of the plate-like precipitates: that is, the high contrast occurred for precipitates along the incident direction of the electron beam, while the lesser contrast occurred for precipitates nearly perpendicular to the incident direction of electron beam. Similar precipitates and contrast have been observed in some metals.32 Most plate-like precipitates were embedded in the Si matrix parallel to the \{111\} plane. Aside from these, we observed very small (<5 nm) precipitates with butterfly-like shade, indicated by the C arrows, all parallel to the (110) plane. We believe the small precipitates exhibited Ashby–Brown’s contrast13, 34 caused by the strain field around the nearly spherical coherent precipitates.

As shown in Fig. 4(c), EDS point-analysis revealed that the plate-like precipitate at point B contained more P than the Si matrix at point A, while there was no difference in Ge content. Unfortunately, quantitative EDS analysis of chemical composition was difficult because we could not focus the electron beam only on the precipitate. Fig. 4(d) shows a lattice image and atomic-structure model of the end of a plate-like precipitate viewed along the [110] direction, revealing an edge dislocation at the end of the precipitate and an extra single lattice plane in the precipitate. The lattice image and the structural model of another precipitate viewed along the [211] direction are shown in Fig. S4(d) in the Supplementary Information. From these results, we conclude that the plate-like precipitates are a P-rich compound and connect semi-coherently with the Si matrix.

In contrast, the lattice image in Fig. 4(e) shows dark spots corresponding to the very small spherical precipitates. Because this lattice pattern matches that of the Si matrix, we conclude that the very small precipitates connected coherently with the Si matrix. Although quantitative EDS analysis was impossible because the precipitates were too small, we adopted a model of a diamond cubic structure with P substituting in half of the Si sites, as shown in Fig. 4(e). Such SiP precipitates with this cubic structure have been found in P-supersaturated Si,35 and a simulated model36 agrees with our observations. Generally, the crystal system of SiP is not cubic but orthorhombic, meaning bulk cubic SiP is not thermodynamically stable. However, the interface energy becomes more dominant as the precipitate size decreases, making cubic SiP stable when it exists as nanoscale precipitates in the Si matrix.

The precipitate size decreased near the grain boundaries, leading to areas where no precipitates formed, as shown in Fig. 4(f) and Fig. S4(e) in the Supplementary Information. We believe that the nanoscale precipitates form by following these four steps: (1) super-heavily P-doped Si crystallizes at a high temperature; (2) the solubility limit of P into Si decreases with decreasing temperature; (3) excess P leaves the Si matrix; and (4) nanoscale P-rich phases naturally precipitate. Near the grain boundaries, the excess P seems to be driven out to the grain boundaries. The presence of this area lacking precipitates near the grain boundaries indicates that a sufficiently large grain size (more than several micrometres) is required to precipitate large amounts of P-rich nanoscale particles.
Conclusions

The polycrystalline Si$_9$Ge$_3$P$_3$ exhibited a significantly higher $z\tau$ of 0.6, more than three times that of optimized bulk Si, as shown in Fig. 1(b). The most important way to maintain high $S\sigma$ in the nanostructure is to ensure that the precipitates coherently or semi-coherently connect with the Si matrix. In the PbTe system, electrons are rarely scattered by such perfect interfacial surfaces, but phonons are scattered. This is an ideal situation for TE materials and the same situation realizes in the present case. In fact, the nanoscale precipitates in the present samples do not strongly influence either $S$ or $\mu_H$ but significantly decrease $\kappa_{\text{th}}$, as shown in Fig. 3(c), (d), and (f). The size and distribution of the nanoscale precipitates could be controlled by adjusting the P and Ge contents, allowing for further enhancement of $z\tau$. Because Si has many advantageous in cost and toxicity compared to Bi, Te, and Pd, used in conventional TE materials, the nanostructured bulk Si prepared in the present study is a promising and scalable TE material.

Experimental

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 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-K$\alpha$ radiation at room temperature. The microstructure and chemical composition of the samples were studied by using scanning electron microscopy (SEM; Hitachi S-2600H) and energy-dispersive X-ray spectroscopy (EDX; Horiba EX-200). The density ($\rho$) of each bulk sample was calculated based on its measured weight and dimensions.

Microstructures were characterized by transmission electron microscopy (TEM). For each TEM observation, each thin specimen was prepared by crushing the bulk sample into powder, 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 (BF) mode (Hitachi H8000), using high-resolution transmission electron microscopy (HRTEM; JEOL 2100), and using HRTEM (JEOL ARM200F) equipped with a silicon drift detector in combination with an ultrahigh-sensitivity energy dispersive X-ray spectroscopy (EDS) instrument.

$\sigma$ and $S$ were measured simultaneously in a He atmosphere at 323–1073 K (ULvac ZEM-3). The Hall coefficient ($R_H$) was measured (Toy Resisteet8300) at room temperature by the van der Pauw method in vacuum under an applied magnetic field of 0.5 T. The bulk samples produced by SPS were characterized using powder X-ray diffraction (XRD; Rigaku RINT2000) with Cu-K$\alpha$ radiation at room temperature. The microstructure and chemical composition of the samples were studied by using scanning electron microscopy (SEM; Hitachi S-2600H) and energy-dispersive X-ray spectroscopy (EDX; Horiba EX-200). The density ($\rho$) of each bulk sample was calculated based on its measured weight and dimensions.

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Notes and references