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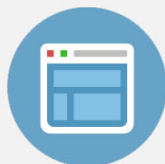
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# Enhanced thermoelectric figure of merit in nanostructured *n*-type silicon germanium bulk alloy

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The dimensionless thermoelectric figure of merit ( $ZT$ ) of the *n*-type silicon germanium (SiGe) bulk alloy at high temperature has remained at about one for a few decades. Here we report that by using a nanostructure approach, a peak  $ZT$  of about 1.3 at 900 °C in an *n*-type nanostructured SiGe bulk alloy has been achieved. The enhancement of  $ZT$  comes mainly from a significant reduction in the thermal conductivity caused by the enhanced phonon scattering off the increased density of nanograin boundaries. The enhanced  $ZT$  will make such materials attractive in many applications such as solar, thermal, and waste heat conversion into electricity. © 2008 American Institute of Physics. [DOI: 10.1063/1.3027060]

Since silicon-germanium (SiGe) alloys have been the only proven thermoelectric materials in power generation devices operating in the 600 °C <  $T$  < 1000 °C range in heat conversion into electricity using a radioisotope heat source,<sup>1,2</sup> much effort has been made to enhance the dimensionless thermoelectric figure of merit  $ZT = (S^2\sigma/k)T$  of SiGe alloys,<sup>3–5</sup> where  $Z$  is the thermoelectric figure of merit,  $T$  is the absolute temperature,  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, and  $k$  is the thermal conductivity. In the 1990s, nanoapproaches were proposed not only to enhance  $S^2\sigma$ , but also to decrease  $k$ ,<sup>6,7</sup> and the approach was experimentally realized in superlattice Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub><sup>8</sup> and quantum dot superlattice PbSe<sub>0.98</sub>Te<sub>0.02</sub>/PbTe<sup>9</sup> materials. Nanostructured SiGe has also been extensively studied, particularly in SiGe/Si superlattice films<sup>10–12</sup> and more recently on Si nanowires.<sup>13,14</sup>

Experimental and theoretical studies on heat conduction mechanisms suggest that an ordered superlattice structure is neither needed nor optimal for reducing the thermal conductivity.<sup>7,15</sup> Hence, random nanostructures with high interface densities can lead to similar  $ZT$  enhancement as in superlattices by strongly reducing phonon thermal conductivity.<sup>16,17</sup> Recently, such a practical technique was reported for making samples of nanostructured *p*-type dense bulk bismuth antimony telluride with a peak  $ZT$  of 1.4 at 100 °C from either alloy ingot<sup>18</sup> or elemental chunks.<sup>19</sup> Even though extensive work has been done in pursuing small-grained SiGe alloy to reduce the thermal conductivity,<sup>20,21</sup> it was found that when the grain size is reduced below microns, accompanying the thermal conductivity reduction is a similar reduction in electrical conductivity and a resulting degradation of  $ZT$ .<sup>20,21</sup> In contrary to the previous results, we report a peak  $ZT$  of 1.3 at 900 °C in *n*-type nanostructured dense bulk SiGe. The *n*-doped SiGe nanopowders were first

prepared by mechanical alloying (ball milling) Si and Ge chunks (99.99%, Alfa Aesar) and P micropowders (99.99% Aldrich). These alloyed nanopowders were then loaded into a graphite die inside a glove box and hot pressed by the direct current induced hot pressing (dc hot press) method into a dense bulk material at temperatures between 1000 and 1200 °C. For our best sample, 2.0 mol % P was added to Si and Ge chunks with a Si/Ge ratio of 80/20, i.e., Si<sub>80</sub>Ge<sub>20</sub>P<sub>2</sub>. Here, we show that the thermal conductivity of the nanostructured SiGe alloys can be reduced to be about 2.5 W/m K, much lower than that (4.6 W/m K) of the conventional bulk alloys with the same overall alloy composition, leading to a peak  $ZT$  of about 1.3 at 900 °C.

The structural properties of the nanopowders and of the bulk samples after the dc hot press were investigated by x-ray diffraction (XRD) with the wavelength of 0.154 nm and by high resolution transmission electron microscopy (HRTEM). Dense bulk disk samples with a diameter of 12.7 mm and a thickness of about 4 mm were cut into several pieces for the characterization of their thermoelectric properties. The thermal conductivity measurement was carried out using a laser flash system (Netzsch LFA 457), and the electrical conductivity and Seebeck coefficient were measured simultaneously on bars of 2 × 2 × 12 mm<sup>3</sup> using an ULVAC ZEM-3 system. For thermal stability testing, samples with a bar or disk form were annealed at 1050 °C for 2 days in air.

Figure 1(a) shows the XRD spectra of the as-prepared nanopowder (bottom spectrum) and of the as-pressed dense bulk sample (top spectrum). It is clear that all the peaks for the as-prepared nanopowders show a weak shoulder on the left side, which can be attributed to the incomplete alloying during the ball milling. Also, all the peaks are broad, indicating the nanosize of the grains. Calculation from the XRD spectra using the Williamson–Hall method<sup>22</sup> ( $\beta \cos \theta / \lambda = 1/d + \xi/2 \sin \theta / \lambda$ , where  $\beta$  is the spectral integral breadth of the diffraction peaks,  $\theta$  is the Bragg diffraction angle,  $\lambda$  is

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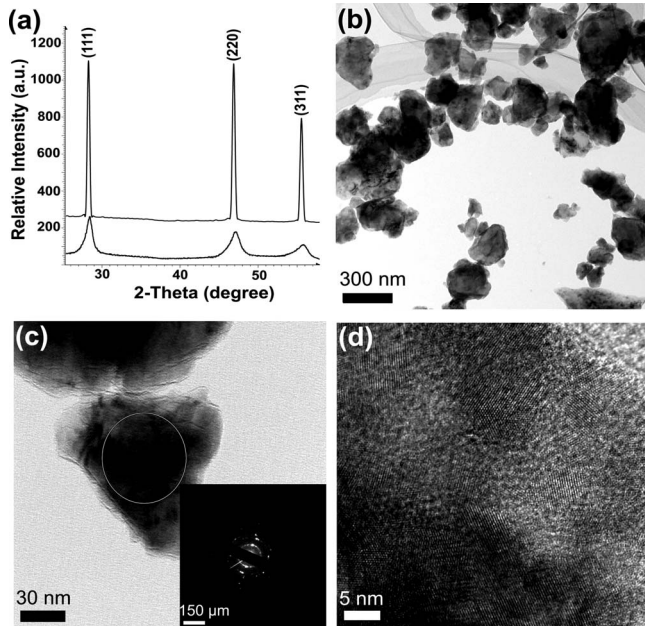


FIG. 1. (a) XRD patterns. (b) TEM images with low, (c) medium, and (d) high magnifications of typical ball milled nanopowders. The inset of (c) shows the selected area electron diffraction pattern.

the incident x-ray source wavelength,  $d$  is the average grain size, and  $\xi$  is the lattice stress in the sample) results in an average grain size of 12 nm. Using the same calculation method, an average of 22 nm was obtained as the grain size for the hot pressed samples, indicating that the grain size after hot press is almost doubled, but still is very small. However, the stress inside the as-pressed samples is much smaller than that of the as-prepared nanopowders, with the  $\xi$  value being ten times lower in the hot pressed samples. This smaller stress is understandable since the hot pressing temperature is above 1000 °C, where the stresses buildup in the nanopowders during the mechanical alloy process are relaxed.

From the TEM picture of the as-prepared nanopowders, shown in Fig. 1(b), we can see that the average particle size of the nanopowder is in the range of 30–200 nm. However, those particles are actually agglomerates of much smaller crystallites. Figure 1(c) shows the TEM image and selected area electron diffraction pattern (inset) of those typical particles, which indicates that the particles are actually composed of many small crystallites. It is also confirmed by HRTEM, as shown in Fig. 1(d), that the sizes of the small crystallites are in the range of 5–15 nm, which is roughly in agreement with the results from the XRD spectra [Fig. 1(a)].

Figure 2(a) shows a low magnification TEM image of the as-pressed dense bulk samples. As we can see, the typical grain sizes are in the range of 10–20 nm, roughly in the same range as the particle size (22 nm) calculated from the XRD spectra. A HRTEM image [Fig. 2(b)] of the as-pressed samples showed that the adjacent grains have a similar crystal structure but different crystalline orientations. We believe that those small grains with random crystalline orientations, as shown in Fig. 2(b), promote phonon scattering much more effectively than the big grains in bulk SiGe materials.

The main advantage of using a nano-SiGe alloy powder for thermoelectric applications comes from the fact that there is a large difference in the mean free path between electrons and phonons: about 5 nm for electrons and 2–300 nm for

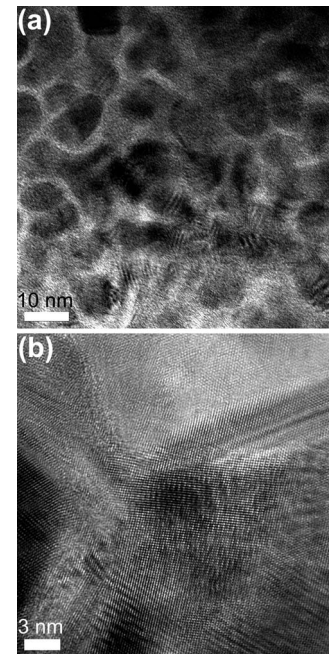


FIG. 2. TEM images with (a) low and (b) high magnifications of the as-pressed nanostructured samples.

phonons in highly-doped samples at room temperature. Thus, nanostructures can significantly reduce the phonon thermal conductivity without creating too much penalty to the electrical conductivity. Figure 3(a) shows the temperature-dependent thermal conductivity of typical  $\text{Si}_{80}\text{Ge}_{20}\text{P}_2$  samples. The data from a radioisotope thermoelectric generator (RTG) sample used for NASA space flight with a typical grain size of 1–10  $\mu\text{m}$  is included as a reference.<sup>23</sup> Figure 3(a) clearly shows that the samples with nanostructures have a much lower thermal conductivity than the reference sample. From the measured electrical conductivity of both samples [Fig. 3(b)], the electronic contribution to the thermal conductivity ( $k_e$ ) can be estimated using the Wiedemann–Franz law with the Lorenz number ( $2.14 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$  for the SiGe system at room temperature). For the reference sample, we obtain  $k_e = 0.77 \text{ W/m K}$  at room temperature with an electrical conductivity  $\sigma = 1.2 \times 10^5 \text{ S/m}$ , whereas for a typical nanostructured dense bulk sample  $k_e = 0.55 \text{ W/m K}$  at room temperature for  $\sigma = 0.85 \times 10^5 \text{ S/m}$ . By subtracting the electronic contribution  $k_e$  from the total thermal conductivity  $k$ , the lattice thermal conductivity ( $k_L$ ) of the nanostructured samples is  $\sim 1.8 \text{ W/m K}$  at room temperature, which is about 47% of that for the reference sample ( $k_L \sim 3.8 \text{ W/m K}$ ) and is mainly due to a stronger boundary phonon scattering in the nanostructured samples.

Figure 3(b) shows a comparison of the temperature-dependent electrical conductivity of the nanostructured samples and the reference. The electrical conductivity of the nanostructured samples is normally lower than that of the reference in the low temperature region, but is similar above 750 °C, although the carrier concentrations for both types of samples are almost the same at room temperature ( $\sim 2.2 \times 10^{20} \text{ cm}^{-3}$  from the Hall effect measurement), indicating a lower electron mobility in the nanostructured samples. Figure 3(c) shows the temperature-dependent Seebeck coefficient. The Seebeck coefficient of the nanostructured samples is similar to that of the reference sample at below 400 °C



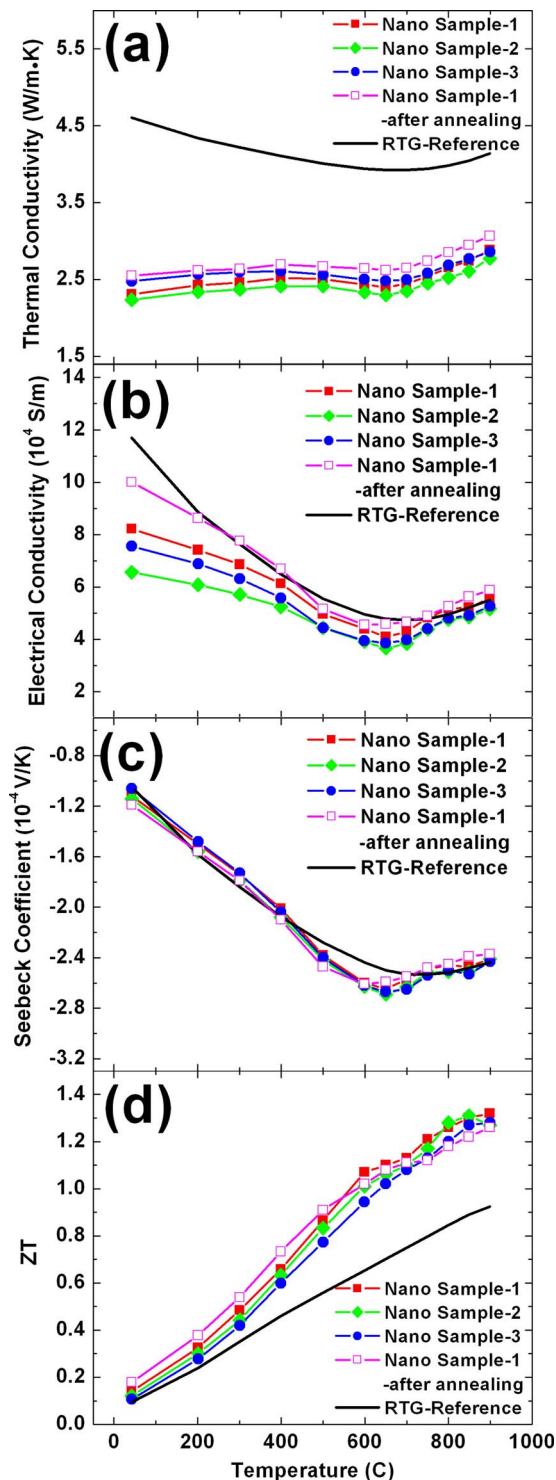


FIG. 3. (Color online) Temperature dependence of (a) the thermal conductivity, (b) electrical conductivity, (c) Seebeck coefficient, and (d) dimensionless  $ZT$  on both as-pressed nanostructured samples (filled symbols) and the RTG reference sample (solid line), and the sample after annealing at 1050 °C for 2 days in air (open squares).

and at above 700 °C, and is higher than that of the reference sample between 400 and 700 °C.

Figure 3(d) shows the  $ZT$  as a function of temperature for the nanostructured samples and the reference. For the nanostructured samples, the  $ZT$  value shows a maximum of about 1.3 at 900 °C which is about 40% higher than that (0.93) of the reference. The significant enhancement of  $ZT$  is mainly attributed to the thermal conductivity reduction,

which is strongly correlated with the nanostructure features in our samples.

For testing the reproducibility, hundreds of samples were made under similar conditions and the typical results are shown in Fig. 3. Thermal stability of the nanostructured samples is a serious concern for thermoelectric materials since thermoelectric devices are required to operate at high temperatures for many years. A thermal stability test was carried out by annealing the nanostructured samples at 1050 °C for 2 days in air and no significant property degradation was found (shown as the open squares in Fig. 3).

In summary, enhanced thermoelectric properties have been achieved in nanostructured dense bulk SiGe alloy. The significant  $ZT$  enhancement that is obtained is the result of a large reduction in the thermal conductivity while maintaining the power factor ( $S^2\sigma$ ). The thermal conductivity reduction is mainly due to an enhanced phonon scattering at the increased boundaries of the nanograins. The enhanced  $ZT$  can lead to new applications, such as solar thermoelectric energy conversion and waste heat recovery.

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