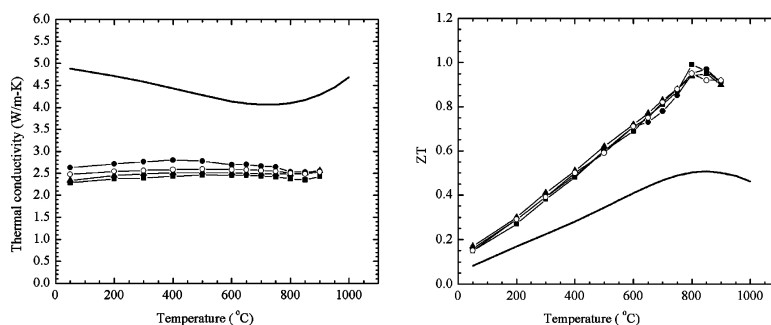# NANO LETTERS

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Enhanced Thermoelectric Figure-of-Merit in Nanostructured p-type Silicon Germanium Bulk Alloys

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ABSTRACT

A dimensionless thermoelectric figure-of-merit (ZT) of 0.95 in p-type nanostructured bulk silicon germanium (SiGe) alloys is achieved, which is about 90% higher than what is currently used in space flight missions, and 50% higher than the reported record in p-type SiGe alloys. These nanostructured bulk materials were made by using a direct current-induced hot press of mechanically alloyed nanopowders that were initially synthesized by ball milling of commercial grade Si and Ge chunks with boron powder. The enhancement of ZT is due to a large reduction of thermal conductivity caused by the increased phonon scattering at the grain boundaries of the nanostructures combined with an increased power factor at high temperatures.

Silicon germanium alloys (SiGe) have long been used in thermoelectric modules for deep-space missions to convert radio-isotope heat into electricity.[1] They also hold promise in terrestrial applications such as waste heat recovery.[2−4] The performance of these materials depends on the dimensionless figure-of-merit $ZT = (S^2\sigma/\kappa)T$,[1,5] where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. Since the 1960s, efforts have been made to improve the ZT of SiGe alloys,[6−9] with the peak ZT of n-type SiGe reaching 1 at 900−950 °C. However, the ZT of p-type SiGe has remained low. Current space-flights run on p-type materials with a peak ZT ∼ 0.5 and the best reported p-type material has a peak ZT of about 0.65.[9,10] In recent years, many studies have shown a significant enhancement of ZT in other material systems via nanostructuring approach to reduce the thermal conductivity by scattering phonons more effectively than

electrons at interfaces in superlattices,[11−15] and in bulk materials, such as lead antimony silver telluride (LAST) alloys,[16] and skutterudites[17] with an operating temperature up to 600 °C. We have been pursuing a nanostructured composite (nanocomposite) approach[18,19] and achieved a 40% peak ZT improvement, from 1 to 1.4, in p-type nanostructured bulk bismuth antimony telluride with an operating temperature up to 250 °C.[20] For applications at around 1000 °C, such as for radio-isotope thermoelectric generators (RTGs) used in space missions, SiGe alloys are among the best options. Past work on microstructuring SiGe alloy showed only a 20% increase in the ZT of p-type SiGe with an optimal grain-size in the 2−5 μm range, but the ZT is expected to decrease further when grain size is further reduced.[21] Here we show, using a low-cost and mass-production ball milling and direct-current-induced hot press compaction process, that a 50% improvement in the peak ZT from 0.65 to 0.95 at 800−900 °C is achieved in p-type nanostructured SiGe bulk alloys. The ZT enhancement is due to a large reduction in the thermal conductivity while maintaining the electron transport properties.

In this work, we observed a significant improvement in ZT with a peak value about 0.95 at 900−950 °C in nanostructured p-type SiGe samples prepared by a dc hot

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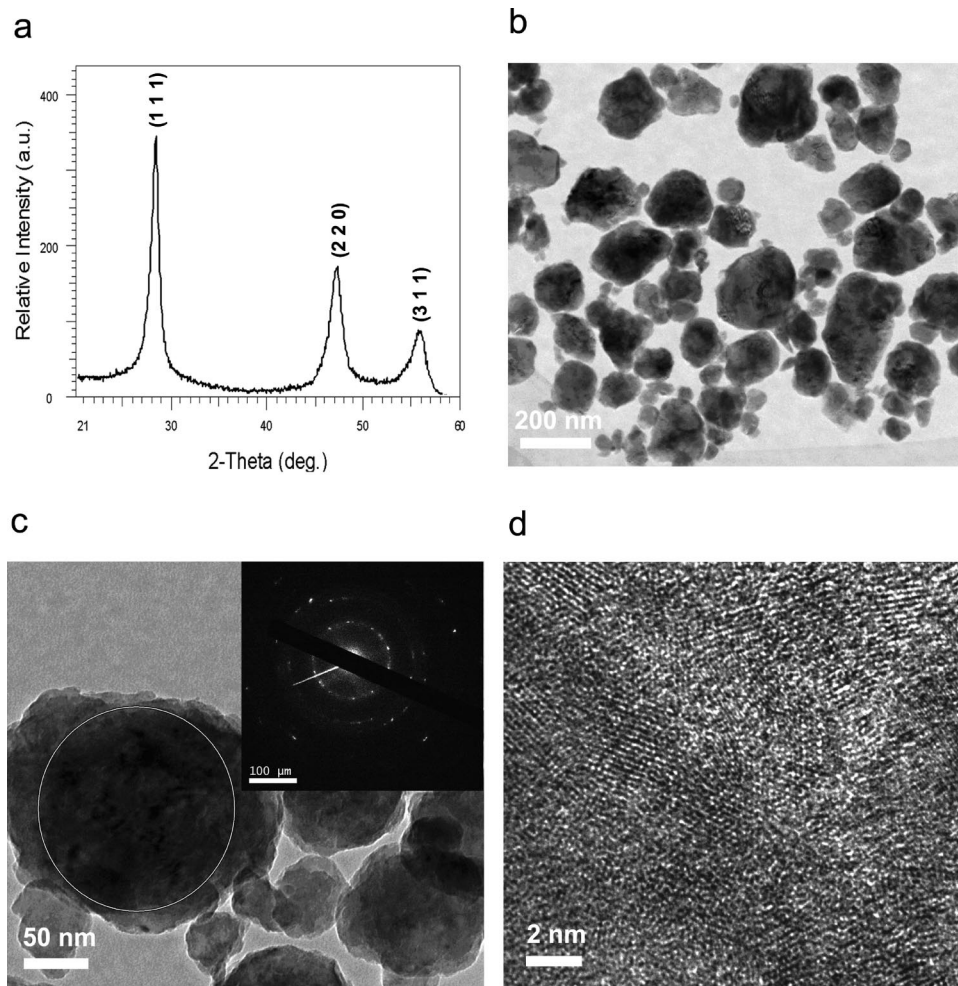# Department of Physics, Massachusetts Institute of Technology.

Figure 1. XRD pattern (a) and TEM images with (b) low-, (c) medium-, and (d) high-magnifications of the ball milled $Si_{80}Ge_{20}$ nanopowders. The inset in panel c is the selected area electron diffraction rings to show the multicrystalline nature of an individual particle.

press of mechanically alloyed SiGe nanopowders, which is about 90% improvement over the RTG samples, and 50% improvement over the previous record.[10] These nanostructured samples consist of polycrystalline grains of sizes ranging from 5 to 50 nm with random orientations. The electrical conductivity, Seebeck coefficient, and thermal conductivity are investigated in the temperature range between 25 and 950 °C. It is found that this ZT enhancement is presumably due to the increased phonon scattering of the grain boundaries and crystal defects formed by lattice distortion with some contribution from the increased electron power factor at high temperatures.

Experimental Section. Nanostructured SiGe alloy particles are prepared by mechanical alloying using a ball mill technique.[22] For fabricating such p-type material, boron (B) powder (99.99%, Aldrich) is added to silicon (Si) (99.99%, Alfa Aesar) and germanium (Ge) (99.99%, Alfa Aesar) chunks in the milling jar. They are then milled for 10−60 h to get the desired alloyed nanopowders. The mechanically prepared nanopowders are then pressed at temperatures of 950−1200 °C by using a dc hot press method for rapid compaction of the nanopowders in graphite dies with a 12.7 mm central cylindrical opening diameter.[20]

The samples were characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS) to study their crystallinity, composition, homogeneity, the average grain size, and grain size distribution of the nano particles. These parameters significantly affect the thermoelectric properties of the final dense bulk samples. The volume mass densities of these samples were measured using an Archimedes' kit. The specimens for TEM were prepared by dicing, polishing, and ion milling of the dc hot-pressed bulk samples.

For the thermoelectric property measurements, the samples are cut into 2 mm by 2 mm by 12 mm bars and also 12.7 mm diameter discs with appropriate thickness. The bar-shaped samples were used to measure the electrical conductivity and Seebeck coefficient, and the disk-shaped samples were used for the thermal conductivity measurements. The electrical conductivity and Seebeck coefficient were measured by commercial equipment (Ulvac, ZEM-3) and the thermal conductivity was measured by a laser flash system (Netzsch LFA 457) from room temperature to 900 °C. To confirm that the nanocrystalline bulk samples are isotropic, cylinder-like thick discs were hot-pressed and cut along perpendicular to the press direction and were then measured.
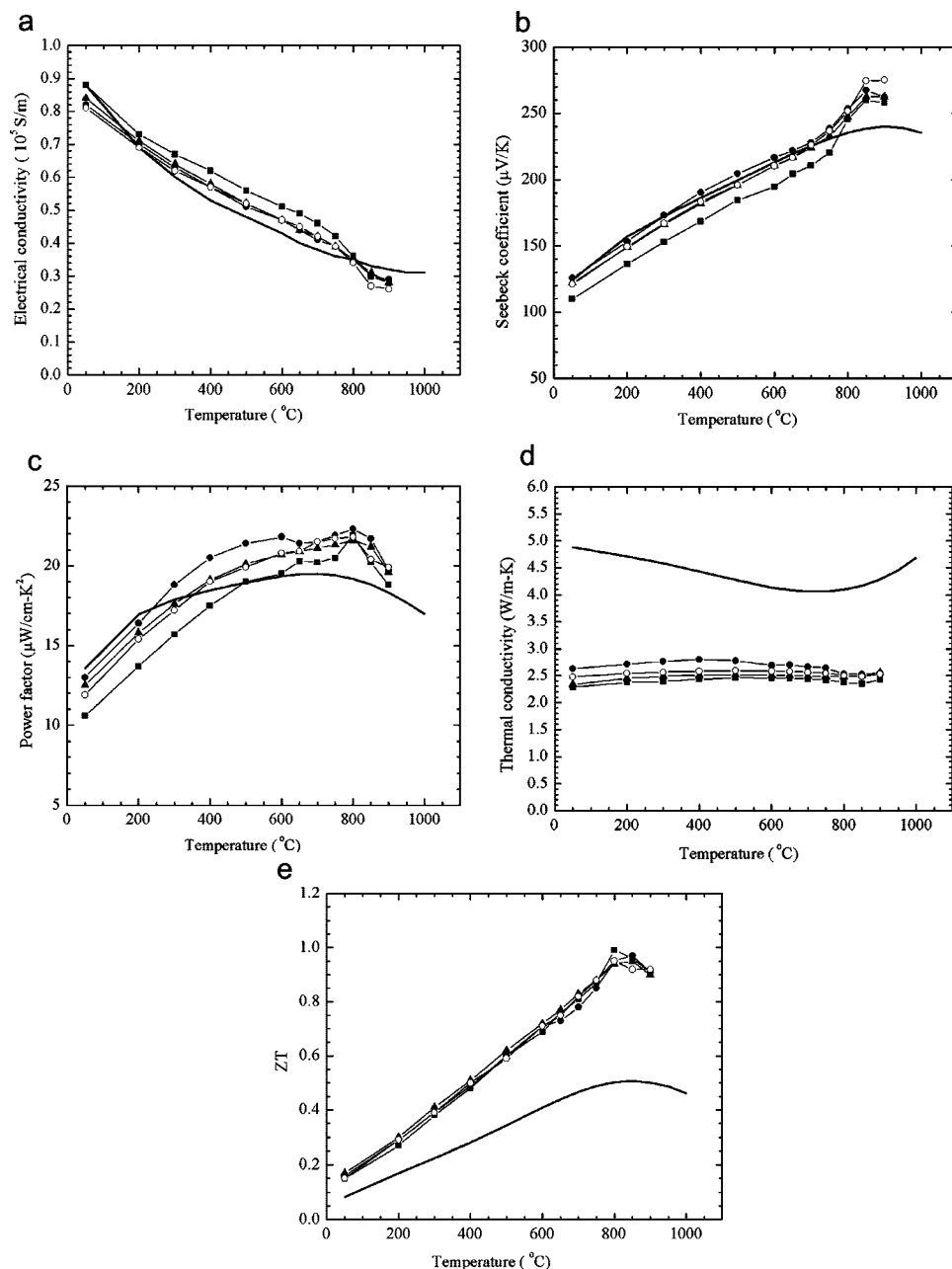
Figure 2. Temperature dependence of (a) the electrical conductivity, (b) Seebeck coefficient, (c) power factor $S^2\sigma$, (d) thermal conductivity, and (e) ZT of three dc hot-pressed nanostructured dense bulk $Si_{80}Ge_{20}$ alloy samples (solid circles, open circles, triangles, and squares) and the 7 day annealed (at 1100 °C) sample in comparison to the p-type SiGe bulk alloy used in RTGs for space power missions (solid line).

The measurement results are in agreement with one another to within 5%, meaning the samples are basically isotropic.

We have repeated the same experimental conditions many times and have confirmed that the peak ZT values are reproducible within 5%.

Results and Analyses. In this paper, we report the results for the temperature dependent thermoelectric properties for a SiGe alloy with an atomic ratio of $Si_{80}Ge_{20}$, doped with boron. Figure 1 shows the XRD pattern (Figure 1a) and TEM images (Figure 1b–d) of the ball milled boron doped $Si_{80}Ge_{20}$ nanopowder. The XRD pattern confirms that the powder is in a single phase and is well matched with those obtained for $Si_{80}Ge_{20}$ alloys.[1] The broadened diffraction peaks indicate

that the sizes of the particles are small. The mean size of the particles, calculated from XRD peaks using the Williamson–Hall method,[23] hover around 15 nm. The low-(Figure 1b) and medium- (Figure 1c) magnification TEM images show that the powder consists of particles ranging from 20 to 200 nm. However, the selected area electron diffraction rings (inset of Figure 1c) obtained inside a single particle indicate that the individual particles are themselves multicrystalline. The high resolution TEM image (Figure 1d) clearly shows that the big particles consist of grains up to 20 nm in size, which agrees fairly well with the size calculated from the XRD spectra (Figure 1a). Furthermore, even inside a single grain many defects still exist (Figure
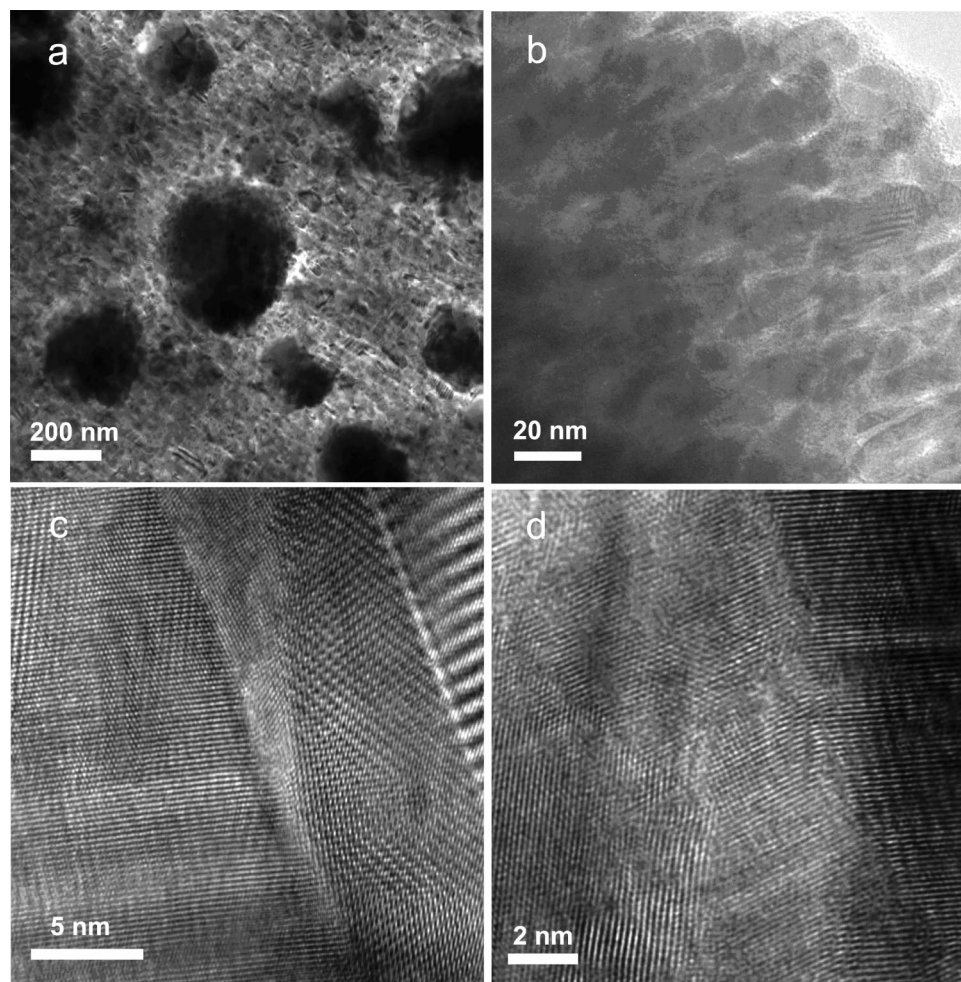
Figure 3. TEM images of the typical dc hot-pressed nanostructured dense bulk samples under (a) low-, (b) medium-, and (c,d) high-magnifications.

1d), because the nano grains were formed by a low temperature mechanical alloying process and not by high temperature melting and solidification.

The solid dots in Figure 2 show the temperature dependence of the electrical conductivity (Figure 2a), Seebeck coefficient (Figure 2b), power factor $S^2\sigma$ (Figure 2c), thermal conductivity (Figure 2d), and ZT (Figure 2e) of the nanostructured dense bulk $Si_{80}Ge_{20}$ (volume mass density 2.88 g/cm^3 measured by Archimedes technique) in comparison to a baseline p-type SiGe bulk alloy sample used in RTGs (solid line) for space power missions. It is clear from Figure 2a−c that the electrical properties were maintained with a power factor comparable to that of RTG samples. Although in different temperature range, the electronic properties (electrical conductivity and Seebeck coefficient) can be below or above that of RTG values, we caution that it is well known that in SiGe samples, dopant precipitation occurs below ∼600 °C and hence low-temperature properties depend on the thermal history of the samples. More important, the thermal conductivity of the nanostructured bulk samples is much lower than that of the RTG sample (Figure 2d) over the whole temperature range up to 1000 °C, which led to a peak ZT of about 0.95 in our nanostructured bulk samples $Si_{80}Ge_{20}$ (Figure 2e). Such a peak ZT value is about 90% improvement

over that of the p-type RTG SiGe alloy currently used in space missions (shown in the figure as the solid line) and 50% above that of the reported record value.[10] The significant reduction of the thermal conductivity in the nanostructured samples is mainly due to the increased phonon scattering at the numerous interfaces of the random nanostructures. Since the total thermal conductivity (κ) contains contributions from both the carriers (κ_{ca}) and phonons (κ_{ph}) ($\kappa = \kappa_{ca} + \kappa_{ph}$), and since the electrical conductivity of the nanostructured bulk sample is similar to that of the RTG sample, the actual phonon thermal conductivity reduction is at least a factor of 2 based on the experimental data shown in Figure 2d.

Since the size and quality of the nanoparticles are essential features in reducing the thermal conductivity to achieve high ZT values, preliminary microstructure studies have also been carried out on the hot-pressed nanostructured bulk samples using TEM (Figure 3). The low magnification TEM image is presented in Figure 3a, which shows dark dots distributed in the background, but both the dots and the background contain small-sized multigrains. A higher magnification TEM image (Figure 3b) shows that the grains are indeed of nanosize up to about 20 nm, similar to the size of the initial powder, indicating no significant grain growth occurring after the dc hot-press process. A detailed crystal structure study

showed no differences in the dark dots and in the background. The observed contrast nonuniformity may be due to the segregation of the dopant (boron). However, the EDS detector in our TEM is not sensitive enough to distinguish the boron concentration. Furthermore, these nanograins are highly crystalline, completely random (lattice planes oriented with different angles) (Figure 3c), closely packed (Figure 3d), and have very clean boundaries (Figure 3c−d), consistent with the measured high volume mass density. The microstructure of the 3 day annealed samples is no different from that of the as-pressed samples.

A serious concern in nanostructured materials is grain growth over an extended period of time at the temperatures at which these materials are generally used. We carried out a thermal stability test by heat treatment of the nanostructured bulk samples at 1100 °C for 7 days and we did not find any noticeable property degradation (represented by the open circles in Figure 2) and grain growth under these conditions. The reason why there is no grain growth at such a high temperature is probably because the grains are similar in size and their random crystalline directions prevent grain growth.

Conclusion. In conclusion, we have applied the nanostructured composite concept[19,20,22] to make p-type nanostructured bulk alloy $Si_{80}Ge_{20}$ to demonstrate a significantly enhanced ZT of about 1 at 800−900 °C. This enhancement in ZT comes mainly from a reduction of the thermal conductivity due to the increased phonon scattering from the high density nanograin interfaces in the nanocomposite. This nanostructure approach is applicable to many other thermoelectric materials that are useful for automotive, industrial waste heat recovery, space power generation, or solar power conversion applications.

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