Supporting Information.

Scalable multi-nanostructured silicon for room-temperature thermoelectrics

Makoto Kashiwagi¹, Yuxuan Liao¹, Shenghong Ju¹, Shota Konishi¹, Asuka Miura¹, Takuma Shiga¹, Takashi Kodama¹ and Junichiro Shiomi¹,²,*

¹. Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo, 113-8656, Japan.
². CREST, Japan Science and Technology Agency, 4-1-8 Kawaguchi, Saitama, 332-0012, Japan.

* Email address: shiomi@photon.t.u-tokyo.ac.jp

1. Measurements procedures of thermal conductivity and electrical properties

When sintering the Si nanowire array to form the nanocomposite film, we configured the sample so that thermal conductivities in both the in-plane and out-of-plane directions and electrical conductivity and Seebeck coefficient in the in-plane direction can be measured. For that, the Si nanowire array on Si substrate was sintered together with another Si substrate with a 300-nm-thick SiO₂ thin film deposited on the surface, which were placed so that the Si nanowire array is in contact with the SiO₂ thin film, as shown in Fig. S1(a) and (b). After the sintering, the sample was etched by deep reactive-ion etching (DRIE) or XeF₂ dry-etching. For the measurement of the thermal conductivity, the sample was etched from the SiO₂ substrate side by XeF₂ dry-etching as shown in Fig. S1(c). Since etching by XeF₂ is highly selective, XeF₂ etches only Si but not SiO₂. Therefore, the SiO₂ layer works as a stopping layer as shown in Fig. S1(d). We then deposited metal-wire on the SiO₂ layer as shown in Fig. S1(e), and measured thermal conductivity by using the 3-omega method. For the measurements of the electrical properties, the sample was etched from the backside of the Si nanowire array by DRIE (MUC21-ASE Pegasus, SPTS) as shown in Fig. S1(f) so that the sample layer is exposed to surface as shown in Fig. S1(g). Then, the electrodes for measurements of the electrical properties were deposited on the sample surface as shown in Fig. S1(h). Electrical conductivity and Seebeck coefficient from room temperature up to 1000 K was measured by using ZEM-3 (ULVAC) with the film-measurement attachment.
2. Energy Dispersive X-ray mapping

Figure S2 shows the images of SEM and energy dispersive X-ray spectrum mapping for silicon (Si), oxygen (O), and silver (Ag). As shown in the figure, the fabricated nanocomposite sample consists mostly of Si. Although some oxygen does exist in the sample, its average content is only 5.9 at. %. Furthermore, as shown in Fig. S2(c), oxygen is mostly concentrated on the surface of the grain exposed to the pore. These characterization suggests that the contamination of the grain boundary with silicon oxide is weak and thus does not significantly reduce the electrical conductivity. The precipitated nanoparticles with diameters below 20 nm was identified to consist of Ag.
3. **Mechanism of nano-porous formation inside nanowires**

As shown in Fig. S3, fabricated nanowire has nanoporous structures. The nanoporous structures were formed due to long-time etching. As illustrated in Fig. S4, as the etching time increases, Ag nanoparticles re-nucleate on the side walls of the nanowires from Ag⁺ ions diffuse in the etching solution. Then the re-nucleated Ag nanoparticles restart the etching and form pores from the side walls. Formation of the nanopores effectively softens the material and make it easier to be squished to a dense material with the high-pressure sintering, and this also makes the resulting grain size significantly smaller than the nanowire diameter. As shown in Fig. S3(c) and (d), due to the high density of pores, distance between the pores is about 10 nm, and therefore the grain sizes after being squished are expected to be about the same size.
Fig. S3 TEM images of a fabricated nanowire with various magnifications. Presence of the internal nanopores can be observed.

Fig. S4 Schematic of formation mechanism of porous Si nanowire by long-time metal assisted etching.

4. **Image analysis for determining structural parameters of the nanocomposite**

As mentioned in the main text, the grain size, pore size, and Ag-particle size in the
nanocomposite were determined from the TEM images by using an image processing method. Here, procedure of the image processing is explained taking an example of determining the grain size from the image shown in Fig. S5. First, the pore areas were excluded as shown in Fig. S5(b). Next, as shown in Fig. S5(c), the grain boundaries were detected from the areas excluding the pore areas. Finally, the diameter of the pore was evaluated from detected grains. Ag particles were also detected in the same way. Here, Ag particle areas were detected based on the contrast caused by the difference in electrical conductivity between Si and Ag. Figure S6 shows distributions of the grain size, pore size, and Ag-particle size estimated by using the image processing. The grain size was distributed from 18 nm to 2 μm, and the average grain size was determined to be 138 nm. Here, the grains, which are under 100 nm, account for about 50%. These grain sizes are much smaller than the diameter of the nanowires, because the nanowires are crushed into 10 nm grains following the characteristic length of the internal nanoporous structures of the nanowires. As shown in Fig. S6(b), the pore size has a bimodal distribution owning to two different length scales of the pores in the nanowire array: the size of the secondary nanopores and the spacing between the nanowires. As shown in Fig. S3(c) and (d), the pore sizes in the nanowires were about several tens of nanometers, and this agrees with the first peak in the pore-size distribution of the nanocomposite. On the other hand, from Fig. 2(a), the spacing between nanowires can be estimated to be about 100 nm, which is consistent with the secondary peak in Fig. S6(b).

![Fig. S5 Procedure of the image analysis. (a) Original image. (b) Exclusion of pores from the original image. (c) Detection of grain boundaries.](image-url)
5. In-plane thermal conductivity measurement

As mentioned in the main text, in this work, we measure thermal conductivity in the in-plane direction $\kappa_\parallel$ by using 3-omega method with multiple-widths heater. We first measured the thermal conductivity in the out-of-plane direction by using 20-μm-width-heater and then obtained $\kappa_\parallel$ by fitting Eq. (4) to the measurement data of 4-μm-width-heater. Fig. S7 shows measurement results and fitting curve when varying anisotropic ratio $\eta$ for Sample 3 as the representative case. As shown in the figure, the best fitting is obtained for $\eta = 0.89$ and variation of 0.01 clearly deteriorated the fitting, and thus, we determined the anisotropic ratio $\eta$ to be 0.89.
Fig. S7 Measurement results by using 4-μm-width-heater and fitted curve with various anisotropic ratio $\eta$ calculated by Eq. (4). Circle plots are the measurement data and dashed lines are the numerical results.

6. Frequency distributions of phonon mean free path (MFP)

Figure S8 shows frequency distributions of phonon MFP considering intrinsic phonon-phonon scattering, impurity scattering, grain boundary scattering, phonon-pore scattering, respectively. Here, MFP of intrinsic phonon-phonon scattering was calculated from first-principles-based anharmonic lattice dynamics. MFP of phonon-impurity scattering was estimated by the following model.

$$A_{\text{imp}} = \frac{A \omega^4}{\nu}. \quad (S1)$$

Here, $\omega$ and $\nu$ are phonon frequency and group velocity, respectively. $A$ is a fitting parameter, and determined so that the thermal conductivity of the reference single-crystal Si sample is reproduced. MFP of grain boundary scattering was calculated by the analytical model in Eq. (4). Here, as shown in Eq. (4), the MFP of grain boundary scattering depends on the thermal boundary conductance (TBC). In this calculation, TBC was set to 40 MW m$^{-2}$ K$^{-1}$. MFP of phonon-pore scattering was calculated by the analytical model in Eq. (3). Figure S8(d) shows the effective MFP obtained by using Matthiessen’s rule. As shown in Fig. S8(b), impurity scattering reduced the effective MFP more than intrinsic phonon-phonon scattering in the high frequency regime, since influence of impurity scattering becomes significant at high frequency regime as can be
understood from Eq. (S1). On the other hands, in the low frequency regime, influence of impurity scattering on MFP is negligible. As shown in Fig. S8(c), phonon-pore scattering does not have frequency dependence, which is apparent from Eq. (3). In contrast, grain boundary scattering strongly depends on frequency, originated from the frequency dependence of the phonon transmissivity at a bonded interface. Comparing these results, MFP of grain boundary scattering was the smallest in most frequency regime, and thus, the value of TBC plays a dominant role in determining the thermal conductivity of the nanocomposite.

**Fig. S8** Frequency distributions of phonon mean free paths (MFPs) (a) MFP of intrinsic phonon-phonon scattering, (b) MFP of impurity scattering, (c) MFP of grain boundary and phonon-pore scattering, (d) effective (total) MFP obtained by Matthiessen’s rule.

**7. Determination of strain**

As stated in the main text, elastic modulus of the nanocomposite sample was significantly reduced from that of the reference single crystal (as shown Fig. S8), and we first investigated the possibility of the strain being present inside the nanograins. This was done by measuring the Raman spectrum. Figure S9 shows the measured Raman spectra of the nanocomposite and
reference single crystal samples. The obtained red shift of the peak at 520 cm$^{-1}$ is shown in the inset. The peak of the nanocomposite was shifted by -0.3 cm$^{-1}$ from peak of the reference. Here, relation between the Raman shift and internal stress is given by $6, 7$

$$
\Delta \omega = -2.0 \times 10^{-9} \sigma,
$$

(S2)

where $\Delta \omega$ is the amount of Raman shift, $\sigma$ is the stress. The internal expansive stress of the nanocomposite is thus evaluated to be 150 MPa. With the elastic modulus of the single crystal 147.50 GPa, the strain was evaluated to be only $1 \times 10^{-3}$.

![Fig. S9](image)

**Fig. S9** Measurement results of Raman spectroscopy. Red and blue lines are the Raman shifts of single crystal reference and fabricated nanocomposite samples, respectively.

8. **Evaluation of elastic modulus of internal crystal grains in nanocomposite**

In this section, we show how to remove the porosity effect on the elastic modulus ($E$) of the nanocomposite following the experimental works of Bellet et al $8$, which shows that $E$ of porous materials is a function of relative density as $8$:

$$
E_p = C E_B \rho^2,
$$

(S3)

where $E_p$ and $E_B$ are $E$ of porous materials and nonporous material (i.e. the solid part), respectively. $\rho$ is the relative density. $C$ is an order-unity constant including the geometric factors, and the value for silicon is around 0.70 $8$. Since $\rho$ and $E_p$ of the nanocomposite are measured as $87.3\% (=100\%-12.7\%)$ and 26 GPa, respectively, the elastic modulus of solid part of the nanocomposite is estimated as 48.9 GPa.
9. Evaluation of thermal boundary conductance (TBC)

As seen in the main text, we discuss that the significant reduction of thermal boundary conductance (TBC) comes from the softening of the grain boundaries, which is estimated as 6.2 GPa. To test the hypothesis, we estimated the TBC of the softened interfaces by atomistic Green’s function (AGF) calculations. The interface structure for AGF calculation consists of three parts (Fig. S10): bulk Si (semi-infinite length) with a modulus of 147.5 GPa is placed on the left (L) and right side of the interface (R), and the 3-nm softened Si with a modulus of 6.2 GPa is put in the center (C). Tersoff potentials are used for the calculation. For the softened Si in the center of the interface, we effectively reduced the parameter of $A$ and $B$ in the Tersoff potential function from 1830.8 eV and 471.18 eV to 132.8131 eV and 34.1812 eV, respectively, which reduces the modulus to 6.2 GPa without changing the lattice constant. The interactions between the atoms of bulk Si and the soft Si are modeled by the mixing rule. The structure is first optimized with the above potential such that the stress tolerance is less than 0.01 GPa and the force tolerance is smaller than 0.005 eV/Å, and then TBC of the interfaces at 300 K is calculated with AGF.

The results show that the TBC of the grain boundary is 39.6 MW m$^{-2}$ K$^{-1}$, which agrees well with the TBC (40 MW m$^{-2}$ K$^{-1}$) required to explain the measured thermal conductivity of the nanocomposite. Therefore, we concluded that the significantly thermal conductivity reduction of the current sample is due to TBC reduction by softening of grain boundaries.

Fig. S10 An effective model structure of the softened interface. The structure is divided into three parts: left (L), center (C) and right (R). Left and right leads are semi-infinite single crystal Si lattice with a modulus of 147.5 GPa. The center part is softened crystal Si (6.2 GPa) with the same lattice constant. In the transverse direction, the periodic boundary conditions were applied for all the three regions.

References


