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Research Update: Phonon engineering of nanocrystalline silicon thermoelectrics

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Nanocrystalline silicon thermoelectrics can be a solution to improve the cost-effectiveness of thermoelectric technology from both material and integration viewpoints. While their figure-of-merit is still developing, recent advances in theoretical/numerical calculations, property measurements, and structural synthesis/fabrication have opened up possibilities to develop the materials based on fundamental physics of phonon transport. Here, this is demonstrated by reviewing a series of works on nanocrystalline silicon materials using calculations of multiscale phonon transport, measurements of interfacial heat conduction, and synthesis from nanoparticles. Integration of these approaches allows us to engineer phonon transport to improve the thermoelectric performance by introducing local silicon-oxide structures. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4962935]

I. INTRODUCTION

The thermoelectric conversion has attracted great attention as a method to convert thermal energy directly to electrical energy. Thermoelectric devices are highly versatile as they are maintenance-free due to absence of moving parts, can generate high power density that does not decrease with miniaturization, and are applicable to a wide range of heat sources. Examples of widely ranging potential applications include energy harvesting power supply for internet-of-things (IoT) sensors, waste heat utilization in automobiles or industrial furnaces, solar thermal power generation,1 charging of mobile devices in remote areas, and co-generation such as topping power generation.2

However, in reality, actual implementations of thermoelectric devices are still limited. One bottleneck is the energy conversion efficiency. The conversion efficiency of the thermoelectric material can be expressed as a function of the dimensionless figure of merit (ZT), which is a material-specific property given by $S^2 \sigma T / (\kappa_e + \kappa_{ph})$, where $S$, $\sigma$, $\kappa_e$, and $\kappa_{ph}$ are the Seebeck coefficient, electrical conductivity, electron thermal conductivity, and lattice (phonons) thermal conductivity. Therefore, improvement of the conversion efficiency requires materials with larger $S$ and $\sigma$, and smaller $\kappa_e$ and $\kappa_{ph}$. Among the great efforts made to independently control the properties, an approach that has been shown to be effective is nanostructuring. The studies of nanostructured thermoelectric materials can be roughly divided into two. One is to strictly control the nanostructures to form quantum-confined or periodic structures3–5 (by using for instance epitaxial growth or lithographic fabrication). The other is to form more random nanostructures in mind of balancing the controllability and scalability for practical use6,7 (by using for instance ball milling and sintering, or precipitation). The former, in addition to the quantum confinement effect, can inhibit phonon transport by interference of phonon waves caused by the periodicity,8,9 which is gaining recent attentions in terms of phononic crystals10–12. The latter, on the other hand, has significantly contributed to improvement of bulk material performance. Many of them aimed at reducing the thermal conductivity by using phonon scattering at the nanostructure interfaces without appreciably interferring the electrical conductivity, using the fact that the phonon mean free paths (MFPs) are in many cases larger than the electron MFPs. This approach does not require strictly controlled structures, and thus, the materials typically consist of nanostructures with distributions in size and...
orientation. This approach has been applied to various compounds, and bulk materials with $ZT$ even more than 2 have been reported for lead-telluride-based structures.

Another major reason for the limited spread of thermoelectrics is the cost of materials and processes. In a typical pi-stacked thermoelectric module, in order to have the temperature gradient across thermoelectric material dominate over other thermal resistances (such as those at contacts or to ambient), the material needs to be sufficiently thick. Therefore, the material cost is larger than those in other energy conversion techniques (such as solar cells), and would limit the industrial implementation as long as heavy or rare elements are used. Conversely, if the material and process costs can be greatly suppressed, even efficiency of conventional materials to this date may be sufficient depending on the type of application. For example, in the energy harvesting for IoT, materials with $ZT = 1$ could generate sufficient power to drive a small communication devices if the module is efficiently integrated. In other words, a key challenge to promote industrial use of thermoelectrics is to achieve the conventional efficiency with inexpensive materials.

Motivated by the progress in nanostructuring and the need for lowering the cost, there is increasing number of works reported to develop bulk nanocrystalline silicon (Si) thermoelectric materials. Si is one of the most abundant species, and its compatibility with the existing silicon technology would reduce the process cost for module integration. Si crystals are in general not a good thermoelectric material due to its high thermal conductivity but those fabricated in form of nanowires have been reported to exhibit $ZT$ values exceeding 0.5 even at around room temperature. Nice review papers are available on various classes of silicon nanostructures and their thermoelectric performances.

Nanocrystalline structures (sketched in Fig. 1), which typically consist of grains with average size of tens to hundreds of nanometers, have advantage in scalability and synthesis costs attributed to facileness of the process. Yet, there are some controllable parameters, such as average grain size, dispersion of the size distribution, and interface (grain boundary) structures. With the recent advances to analyze phonon transport properties, it has become possible to predict the effect of the controllable parameters on the nanocrystalline thermal conductivity, which has enhanced the designability of thermoelectric materials. In this article, we review a series of our published works exercising the approach to enhance the thermoelectric performance of Si-based nanocrystalline thermoelectrics, with particular focus on the effect of oxygen inclusion, which in principle can be done without any additional cost.

II. ENGINEERING PHONON TRANSPORT IN NANOCRystALLINE MATERIALS

Understanding the phonon transport in nanocrystalline structure is the basis of controlling its thermal conductivity. The general mechanism of the reduction can be explained from the viewpoint of phonon gas kinetics. As shown in Fig. 1(a), when the grain size is significantly larger than the phonon MFP, because most of the phonons are scattered by other phonons before reaching the grain boundary (diffusive phonon transport), heat conduction within the grains can be considered to be the same as that in the bulk single crystal. On the other hand, as shown in Fig. 1(b), in case the grain size is significantly smaller than the phonon MFP, because phonons are scattered by interface without being scattered by other phonons (ballistic phonon transport), the effective thermal conductivity of a grain is smaller than that of the bulk single crystal. This is called the (classical) size effect, which is a common feature of transport coefficient often discussed in terms of Boltzmann transport. Since electron MFP of semiconductors is generally smaller than phonon MFP, by making the grain size larger than the former and smaller than the latter, it should be possible to selectively inhibit phonon transport without appreciably sacrificing electron transport, leading to enhancing the ratio of electrical to thermal conductivity.

Although the above concept is simple, in reality, the mechanism of heat conduction is much more complicated owning to strong mode-dependence of phonon transport properties. Phonon MFP greatly depends on the frequency and polarization, and for instance, phonon MFP in single crystal Si can vary by several orders of magnitude. Therefore, actual heat conduction in nanocrystalline Si consists of mixture of the above diffusive and ballistic phonon transport as shown in Fig. 1(c), which is addressed as “quasi-ballistic” or “diffusive-ballistic” transport. In addition, phonon
transmission at the interface can also strongly depend on frequency and polarization.\textsuperscript{29–33} Understanding of such mode-dependent phonon transport properties is the key to develop nanocrystalline thermoelectrics.

There has been a great advance over the last decades in techniques to practice phonon-engineering aiming to provide design guidelines of structure or materials based on the physics of phonon transport. Figure 2 summarizes the integrated approach coupling theoretical/numerical calculations, property measurements, and structure fabrication/synthesis. It is important to note that the coupling here is done not only at macroscopic level but also at microscopic level to develop materials on the basis of rules and principles. Instead of characterizing the material in terms of thermal conductivity, calculating and measuring phonon-mode-dependent contribution to thermal conductivity (thermal conductivity spectrum) helps us understand and design the material from the above multiscale viewpoint. Furthermore, techniques to fabricate/synthesize and measure a model sample that separates interface effect from internal (inside the grains) effect help us understand and design interfacial structures and heat conduction.
Approach to develop nanostructured thermoelectric materials combining theoretical/numerical calculations, structure fabrication/synthesis, and property measurements at both microscopic and macroscopic levels.

III. MULTISCALE PHONON TRANSPORT ANALYSIS

Calculations of the phonon transport properties and effective thermal conductivity in bulk nanostructured materials from microscopic viewpoint require a system that is too large to be fully solved by first principles. On the other hand, the value of thermal conductivity sensitively affects the thermoelectric figure-of-merit, and high computational accuracy is indispensable. To balance these two points, we have developed a multi-scale phonon transport calculation method that starts from the first-principles calculations. A flow chart of the method is shown in Fig. 3.

First, the interatomic force constants are obtained by first-principles calculation using the density functional theory. Based on this, mode-dependent phonon transport properties (density of states, group velocities, and relaxation times) are calculated using (anharmonic) lattice dynamics method. In case of disordered crystals, molecular dynamics method using the anharmonic interatomic force constants (i.e., potential functions) is useful. The molecular dynamics method, being a stochastic method, is noisier than the deterministic lattice dynamics method, but it is more suited to handle a non-uniform structure being a real space method. In addition, molecular dynamics methods that solve the actual molecular trajectories have merits in handling larger displacements at high temperatures compared with lattice dynamics that is based on perturbation theory. The obtained phonon transport properties are then inputted into mesoscopic approaches such as Monte Carlo methods. Monte Carlo methods have advantage in adaptability to complex interface shapes in nanocrystalline materials and also in possibility to stochastically introduce transmission and reflection of phonons at the interface (grain boundaries).

We here omit explanations of the part to calculate (single-crystal) phonon transport properties because it has been described in detail in previous review papers. It should be noted that the single-crystal phonon transport properties are now also measurable in experiments. While measurements of phonon dispersion relations using the inelastic neutron scattering spectroscopy and inelastic X-ray scattering spectroscopy have been possible for long time, the recent improvement in their resolutions has made it possible to obtain the phonon lifetimes (or relaxation time) from the spectrum profiles. There are also transient measurements in the time domain using the femtosecond X-ray free-electron laser pulses. In addition, there have been advances in methods to obtain phonon MFPs from the size effect of thermal conductivity. Mainly using pump-probe thermoreflectance methods, by varying the size or heated region within the quasi-ballistic regime, contribution from the phonons with MFPs larger than the heated region is suppressed, resulting in
FIG. 3. Flow chart of the multiscale phonon transport calculation.

reduction of the apparent (measured) thermal conductivity, from which MFPs-dependent thermal conductivity can be extracted. The method can now be applied also to materials with short MFPs, by reducing the size of heated spot to several tens of nm.

We here explain the mesoscopic Monte Carlo simulations that relate the single-crystal phonon transport properties to nanocrystalline thermal conductivity. One way to make the calculation affordable is to solve phonon transport in view of Boltzmann transport assuming phonon transport inside the grain to be indifferent from that of single crystals and describing phonon transport across the interface in terms of mode-dependent transmission function or probability. There are various ways to solve Boltzmann transport equation but Monte Carlo method has an advantage in facileness to handle complicated surfaces and interface shapes.

For phonon transport, the following linearized Boltzmann transport equation with relaxation time approximation is commonly used:

\[ \frac{\partial f_s(\omega, \mathbf{r})}{\partial t} + v_s(\omega) \mathbf{e} \cdot \nabla_r f_s(\omega, \mathbf{r}) = -\frac{f_s(\omega, \mathbf{r}) - f_0(\omega, T)}{\tau_s(\omega, T)}. \]  

(1)

Here, \( f(\omega) \) is phonon distribution function, \( f_0 \) is the Bose-Einstein distribution function, \( \mathbf{e} \) is the unit vector in the direction of phonon transport, and \( s \) is the branch index. By plugging in the phonon group velocities \( v(s) \) and relaxation times \( \tau(s) \) calculated by the above lattice dynamics method, simulations with non-empirical phonon transport properties can be realized. There are also ways to solve the collision terms more rigorously by directly combining the equation with lattice dynamics; however, the relaxation time approximation is known to be reasonable unless the thermal conductivity is very high (as high as carbon nanotubes). In the Monte Carlo simulations, phonons are transported according to their group velocity and scattered by other phonons (phonon-phonon scattering) inside the grain with probability of \( P = 1 - \exp[-\Delta t/\tau(\omega)] \), within the duration \( \Delta t \). When a phonon is scattered, the phonon states (frequency, polarization, group velocity, and direction) are reset to the equilibrium distribution of the local temperature. When the phonon reaches the
interface, the phonon is transmitted or reflected following the given transmission probability in the direction stochastically determined by the scattering characteristics (e.g., specular or diffusive). By using the energy-based variance-reduced Monte Carlo formulation, the simulations can be greatly speeded up, enabling direct calculations of mesoscale systems.

Another way to calculate the phonon transport of mesoscale system is, instead of solving for the phonon distribution function, to calculate one by one the probability (transmission probability $T_p$) for phonons to transmit from one side to the opposite side of the system in a “ray tracing” manner.\(^\text{39}\) Thermal conductivity in this case is given by Landauer formula,

$$\kappa_{\text{ph}} = \frac{3}{2} \sum_\text{ks} C_{\text{ks}} v_{\text{ks}} \int_0^{\pi/2} T_{\text{P,ke}}(\theta) \cos \theta \sin \theta d\theta. \quad (2)$$

If we assume phonon-phonon scattering (or any internal scattering) and the interface scattering are independent events, the calculation becomes even simpler and the computational time is greatly reduced. First, by calculating $T_p$ from the ray-tracing simulations without any internal scattering, MFP of the boundary scattering process ($\Lambda_{\text{bd}}$) can be obtained as,

$$\Lambda_{\text{bd}} = \frac{3}{2} L \int_0^{\pi/2} T_p(\theta) \cos \theta \sin \theta d\theta. \quad (3)$$

Then, by incorporating the influence of the scattering internal by using Matthiessen rule, the total effective mean free path can be obtained as,

$$\Lambda_{\text{int}}^{-1} = \Lambda_{\text{bd}}^{-1} + \Lambda_{\text{int,ks}}^{-1}, \quad (4)$$

where $\Lambda_{\text{int}} = (vT)$ is the mean free path of internal scattering, i.e., single-crystal phonon MFPs. Finally, by plugging this into solution of Eq. (2), thermal conductivity and its spectrum (mode-dependence) can be obtained.

In both above approaches, phonons reaching the interface are reflected or transmitted in accordance with the interface transmission probability. This interface transmission probability of a specific interface can be calculated by the atomistic Green’s function method, lattice dynamics method, wave packet method, or non-equilibrium molecular dynamics method.\(^\text{32,60}\) However, these methods require input of the specific atomic structures at the interface, while the interfaces in the actual nanocrystalline materials formed for instance by sintering are diverse, complex, and difficult to generalize, particularly in the scope to introduce second phase to the interface such as SiO$_x$. Therefore, at this stage, it seems more reasonable, at least in the mind of material design, to treat the interface phonon transmission probability as variable parameter and experimentally measure them for each system. Yet, modelling efforts should be made to reduce the number of the parameters, preferably to a scalar quantity.

A compromising solution here is to adopt a model that describes the interface transmission function as a simple frequency-dependent function,\(^\text{61,62}\)

$$t(\omega) = \left(\frac{\gamma \omega}{\omega_{\text{max}}} + 1\right)^{-1}. \quad (5)$$

The model captures the first-order feature of the frequency dependence. The constant parameter $\gamma$ here has a one-to-one relation with the thermal boundary conductance (TBC) (inverse of thermal boundary conductance) sketched in Fig. 4(a). Therefore, for a given value of TBC and grain geometry, if we assume the value to be the same for all the grain boundaries, effective thermal conductivity of nanocrystalline material can be obtained.

Calculation results for nanocrystalline Si are shown in Figs. 4(b) and 4(c).\(^\text{59}\) One important finding is that the thermal conductivity of nanocrystalline Si is sensitive to average grain size and TBC at the grain boundary but it is insensitive to the grain-size distribution. Figure 4(b) shows that thermal conductivity of nanocrystalline Si with large standard deviations in grain size ($\sigma = 0.35$) is nearly the same as that of simple cubic structure ($\sigma = 0.0$) as long as the average grain size is the same. Since this comes from the fact that $\Lambda_{\text{bd}}$ is insensitive to the grain size distribution, it also applies to other materials, and thus greatly simplifies the design of nanocrystalline materials. Figure 4(c) shows the effective thermal conductivity of nanocrystalline Si as a function of average
FIG. 4. (a) Illustration of nanocrystalline Si and the thermal boundary conductance (or resistance) at the gain boundary. (b) Thermal conductivity of simple cubic model and nanocrystalline Si with grain size distribution with standard deviation $\sigma = 0.35$. The calculation results are shown for the cases of TBC = 100 and 1000 MW m$^{-2}$K$^{-1}$. The results are compared with the experiments of nanocrystalline Si by Wang et al.\textsuperscript{61} (c) Thermal conductivity of nanocrystalline Si calculated by Monte Carlo (ray tracing) simulations as functions of average grain size ($D$) and thermal boundary conductance at the grain boundaries.\textsuperscript{59}

Grain size and TBC. From this, we obtain a guideline for material development: nanocrystalline Si with average grain size of a few tens of nanometers and TBC of a few hundreds of MW m$^{-2}$ K$^{-1}$ would reduce the thermal conductivity well below 10 W m$^{-1}$ K$^{-1}$ and make it approach the value of amorphous Si.
IV. ENGINEERING PHONON TRANSPORT AT SINTERED INTERFACES

As mentioned above, the physical structure and chemical composition of the interface (grain boundary) and the resulting thermal boundary conductance or phonon transmission function strongly depend on the fabrication/synthesis method and detailed process conditions (temperature, pressure, surface treatment, etc.), and thus, characterization of interfacial thermal transport should be based on experimental measurements. However, it would be extremely difficult to extract the local thermal boundary conductance at a grain boundary directly from the nanocrystalline samples produced for instance by spark plasma sintering (SPS). One solution is to simulate the grain boundary using a model experiment of a planar interface formed by sintering two planar materials, i.e., effectively the same process as the actual particle sintering. Then TBC at the planar interface with quasi-infinite cross section can be measured for instance by the time-domain thermoreflectance (TDTR) method.63–65

In the TDTR method, a metal layer deposited on the sample surface is pulse-heated by a pulsed pump laser, and the temperature response is measured through the surface reflectivity that depends on the temperature (thermoreflectance) by a pulsed probe laser. Obtained time history of surface temperature is then fitted by a physical model such as the heat conduction equation with unknown (target) thermal properties as parameters. By pulsating or modulating (used for lock-in) the laser at high frequency (typically tens of megahertz), the thermal penetration depth becomes small enough that interfacial thermal resistance is detectable (becomes a significant fraction of the overall thermal resistance). However, for this, the sample needs to satisfy a few requirements. First, the interface needs to be located within the thermal penetration depth from the surface, i.e., the Si layer on the surface side needs to be thin. Second, in order to ensure the consistency with the physical model, the thin Si layer must be highly planar and uniform.

To satisfy these conditions, a new process has been developed using silicon on insulator (SOI) substrate and selective etching. An SOI consists of Si-thin-film/SiO$_2$-layer/Si-handle-layer with high planarity and uniformity.66–67 As shown in Fig. 5(a), the Si-thin-film of the SOI is bonded to a Si wafer by spark plasma sintering (SPS). Then by etching first the handle-Si layer by KOH, and next the SiO$_2$-layer by HF, we obtain the desired structure consisting of only Si-thin-film sintered to the Si wafer. The planarity and uniformity of the interface can be confirmed in the TEM image shown in Fig. 5(b). The validity of the developed process and the TDTR measurements has been tested for interfacial layer consisting of SiO$_2$ with thickness ranging from a few nanometers to tens of nanometers, formed by using Si wafers with SiO$_2$ layers grown on the surface. The measured total TBC, which includes thermal resistance of amorphous SiO$_2$ and TBC of Si/SiO$_2$ interface, agreed well with those obtained from previous experiments and numerical simulations.68–70

Using this process, various interface structures were obtained by varying the sintering temperature ($T_s$), pressure, surface chemical treatments, and crystal orientations. Figure 6 shows TEM images of the obtained interfacial structures and their TBC measured by the TDTR method. Dependence on the pressure is not shown here as it was found not to appreciably influence the TBC at least within the varied range. For all the cases shown here, wafer surfaces are cleaned by HF etching prior to the sintering but small amount of oxygen is expected to be present due to regrowth of oxide layer (~2 Å) during rinsing with ultrapure water and brief exposure to ambient air.

When sintered at relatively low temperature, SiO$_x$ precipitate-like non-spherical nanoparticles are formed at the sintered interface, where the structure and composition of the nanoparticles strongly depend on the sintering temperature $T_s$. Figure 6 shows the cases of interface with matched crystal orientation: (100) surface of SOI and (100) surface of Si are bonded with the same crystal orientation. When $T_s = 750{\degree}C$ (a), the nominal size of the particle is about 6 nm x 3 nm (in the direction parallel and normal to the interface, respectively) and the average oxygen concentration measured by EDS is about 7 at. %. For $T_s = 950{\degree}C$ (b), the size is about 15 nm x 10 nm, and the concentration is about 3 at. %. The TEM images show that the SiO$_x$ nanoparticles consist of crystalline lattices despite that the oxygen concentration is far above the solubility limit of oxygen in silicon crystal (ppm order).71 Therefore, we do expect significant lattice deformation, which may contribute to scatter phonons. The amount of oxygen atoms in the SiO$_x$ nanoparticles approximately corresponds to that of 2 Å-thick native oxide layer (with 40 at. % oxygen) on the wafer surface. In
case of higher $T_s (\approx 1100 \, ^\circ C)$ (c), the SiO$_x$ nanoparticles are no longer present and pure Si-Si interface is formed with lattice deformation and local strains. From these observations, it is likely that the SiO$_x$ nanoparticles are formed during the plasma sintering (with kA-order-current) by locally breaking down the native oxide layer into discontinuous patches and thermally diffusing oxygen.
FIG. 6. Thermal boundary conductance at Si–Si interface sintered at different temperatures. Results are shown for the case with matched crystal orientation ((100) surface bonded with (100) surface) and the case with crystal orientation mismatch ((100) surface bonded with (111) surface). (a)-(d) shows the TEM images at the Si–Si interface structures. For each sample, the measurements were performed at different locations and times on the surface. The averaged values are denoted with the larger markers, and the extent of data fluctuation is indicated by plotting all the data with smaller markers. The fluctuation is large particularly for the case of (100)/(111) interface at 1100 °C because the sensitivity of the TDTR signal to the value of TBC is small in this case. Reproduced with permission from Sakata et al., Nano Energy 13, 601 (2015). Copyright 2015 Elsevier.

into the Si lattices near the interface. Since the diffusion length should scale with kinetic energy, the nanoparticle size increases with $T_s$.

The formation of the nanoparticles at the interface was found to give rise to significant tunability of TBC at the Si–Si interface. First, in the case of pure Si–Si interface without nanoparticles ($T_s = 1100$ °C), despite the presence of lattice deformation, TBC is larger than 10 GW/m² K (more than 10% of thermal conductance of single crystal Si of a few nanometer thick). Note that exact value in this case cannot be determined because the sensitivity of the TDTR signal to the value of TBC is not sufficient. Now, by formation of the crystalline SiO$_x$ nanoparticles, TBC is significantly reduced. Furthermore, the value of TBC sensitively decreases with decreasing size and increasing oxygen-concentration of the nanoparticles; TBC values for $T_s = 950$ °C and 750 °C differ by a factor of 2 ($9.2 \times 10^2$ MW m$^{-2}$ K$^{-1}$ and $4.4 \times 10^2$ MW m$^{-2}$ K$^{-1}$, respectively).

Further reduction of TBC can be realized by introducing a mismatch in the crystal orientation. Note that in the actual nanocrystalline materials formed by sintering, grains are expected to be distributed with random crystalline orientations, and thus, the crystal orientations at a grain boundary are likely to mismatch. As shown in Fig. 6, in the case of bonding (100) surface and (111) surface, TBC is significantly reduced by the mismatch of crystalline orientation for all $T_s$. The TEM image of the interface structure with $T_s = 810$ °C (d) shows that the “nanoparticles” in this case is much thinner (∼1 nm thick) and the oxygen concentration is somewhat higher (14 at. %) compared with those formed at the (100)/(100) interface with similar sintering temperature ($T_s = 750$ °C), while the total amount of oxygen atoms remains the same. The value of TBC in this case is $1.9 \times 10^2$ MW m$^{-2}$ K$^{-1}$, which is as small as thermal conductance of a uniform amorphous SiO$_2$ film with thickness of 7 nm.

The above results suggest that contribution of local crystalline SiO$_x$ structure and lattice mismatch is far more efficient than the amorphous SiO$_2$ layer even with smaller oxygen concentration. The fact that SiO$_x$ are localized in the form of nanoparticles or patches is beneficial for thermoelectrics, because the electrons can diffuse along the continuous bonds through the gap between the nanoparticles. Quantitatively, the measurements show that TBC at the Si–Si
interface can be controlled by an order of magnitude using the SiO$_x$ interfacial structure. This means the design guideline obtained in Section III by multiscale phonon transport calculations “TBC of a few hundreds of W m$^{-2}$ K$^{-1}$” is possible by means of SiO$_x$ precipitates at the grain boundary.

V. SYNTHESIS OF NANOCRystALLINE SILICON THERMOELECTRICS WITH CONTROLLED OXYGEN CONTENT

The above analysis suggests that Si nanocrystalline material with average grain size of a few tens of nanometers would reduce thermal conductivity to less than 10 W m$^{-1}$ K$^{-1}$ if oxygen content is appropriately controlled. In Si, most of the contribution to electrical conductivity comes from electrons with mean free paths less than 20 nm even at 127°C, and thus, a few tens of nanometers is an appropriate size to reduce lattice thermal conductivity while retaining electrical conductivity. This has been put into practice by synthesizing nanocrystalline materials using Si nanoparticles with variable oxygen content on the surface. To limit the average grain size to a few tens of nanometers after grain growth, we have chosen Si nanoparticles with diameter of about 6 nm produced by plasma CVD (PECVD) method. Use of PECVD nanoparticles has a merit in obtaining a narrow size distribution. In addition, by terminating the Si nanoparticle surface with chlorine atoms and gradually oxidizing the surface (substituting the chlorine atoms with oxygen atoms) by exposing them in air, the oxide-shell thickness can be controlled through the exposure time. The PECVD method also has an advantage in realizing doping (here n-type with phosphorus) with homogeneous distribution and high concentration.

A bulk material was obtained by plasma-sintering the Si/SiO$_x$ core-shell nanoparticles at 960°C. We here show the case of 4-h exposure (oxidization), which resulted in the best thermoelectric performance among the other exposure times. The density of the sample is about 96% compared with that of bulk single-crystalline Si. As shown in Fig. 7, the TEM image shows that in addition to the nanocrystalline structures [Fig. 7(a)], significant fraction of the material consists of amorphous SiO$_x$ [Fig. 7(b)]. The image of the nanocrystalline region shows that significant grain growth takes place during the sintering, and the average grain size is about 30 nm. The EDS analysis shows that small amount of oxide precipitates in the nanocrystalline regions. The amount of other impurities such as chloride and metal was less than 2%. The amorphous SiO$_x$ regions have sizes of order of a micrometer and occupy as much as 30% in area, though the remaining nanocrystalline regions are still majority and geometrically percolated. The EDS analysis identified that the amorphous region consists of SiO$_x$ (25 at. % oxygen), presumably formed by the viscous flow driven by surface tension force between SiO$_x$ and Si during the sintering.

Figure 8(a) shows that the thermal conductivity of the material is smaller than 6 W m$^{-1}$ K$^{-1}$ at all temperatures. The temperature dependence is very small, and the thermal conductivity is as low as 4.8 W m$^{-1}$ K$^{-1}$ at 1000°C, a value comparable to that of SiGe. While the leading mechanism of the reduction should be phonon scattering at the grain boundaries in the nanocrystalline region, the amorphous region also contributes significantly to the reduction. The impact can be estimated by using the effective medium theory, where the effective thermal conductivity $\kappa_{\text{eff}}$ is expressed as,

$$\kappa_{\text{eff}} = \frac{\kappa_a(1 + 2\alpha) + 2\kappa_c + 2\varphi[\kappa_a(1 - \alpha) - \kappa_c]}{\kappa_a(1 + 2\alpha) + 2\kappa_c - \varphi[\kappa_a(1 - \alpha) - \kappa_c]} \kappa_a,$$

(6)

where $\kappa_c$ is the thermal conductivity of Si nanocrystalline, $\kappa_a$ is thermal conductivity of amorphous SiO$_x$ (estimated here with bulk SiO$_2$ value), $\varphi$ is the volume fraction of SiO$_x$, and $\alpha$ is a dimensionless parameter defined as $\alpha = r_{\text{TRB}}/(d/2)$. Here, $d = 1 \mu$m is the effective diameter of SiO$_x$ and $r_{\text{TRB}} = R_{\text{BB}}$, where $R = 2.3 \times 10^{-7}$ m$^2$ K W$^{-1}$ is the thermal boundary resistance between Si and SiO$_2$. The calculation estimates that the presence of the amorphous regions further reduces thermal conductivity of nanocrystalline by about 30%.

Figure 8(c) shows the temperature dependence of the electrical conductivity. The temperature dependence is weak but it moderately decreases with increasing temperature below 690°C due to increase in electron-phonon scattering rates, a typical trend of degenerately doped semiconductors. Above 690°C, the electrical conductivity moderately increases with temperature due to the kinetics.
FIG. 7. TEM images of the 4-h-oxidation sample, which consists of (a) nanocrystalline Si regions and (b) amorphous SiO$_x$ regions. (c) Low magnification TEM of the overall structure and (d) the picture of the Si-based nanocrystalline thermoelectric material in a form of a pellet. Note that the magnified views show the representative structure of each region and are not taken at the exact locations pointed by the arrows. Reproduced with permission from Miura et al., ACS Appl. Mater. Interfaces 7, 13484 (2015). Copyright 2015 American Chemical Society.

of dopant precipitation related to the retrograde solid solubility of phosphorus in silicon. As the temperature increases, the phosphorus trapped at the grain boundaries diffuses back into the silicon grains and increases the carrier concentration.

The carrier concentration of this sample obtained by Hall-effect measurement is $1.20 \times 10^{20}$ cm$^{-3}$ at room temperature. The resulting carrier mobility $18.5$ cm$^2$ V$^{-1}$ s$^{-1}$ is significantly smaller than bulk Si but is close to that of the optimized sample in Bux et al. and Schierning et al. despite the presence of the amorphous oxide region, attributed here to the geometrical percolation of the nanocrystalline region.

Figure 8(d) shows the temperature dependence of Seebeck coefficient, which is negative as the material is n-type semiconductor. With increasing temperature, the absolute value of Seebeck coefficient increases below 690 °C and decreases above 690 °C. This temperature dependence is qualitatively opposite from that of electrical conductivity but since the magnitude of the variation is much larger, the temperature dependence of the power factor mostly follows that of Seebeck coefficient: increases with temperature until 690 °C and then saturates (Fig. 8(e)). Figure 8(f) shows the temperature dependence of $ZT$, which reaches as high as 0.58 at 850 °C.

The comparison of the thermoelectric properties between our work and the previous works shows that the electrical conductivity in our work is lower than those in previous works.
FIG. 8. Temperature dependences of (a) thermal conductivity, (b) lattice thermal conductivity (extracted using Wiedemann Franz law), (c) electrical conductivity, (d) Seebeck coefficient, (e) power factor, and (f) $ZT$ of Si-based nanocrystalline thermoelectric materials fabricated by sintering nanoparticles oxidized in air for 4 h (red open circle) compared with those of Refs. 15–18. Reproduced with permission from Miura et al., ACS Appl. Mater. Interfaces 7, 13484 (2015). Copyright 2015 American Chemical Society.

for the entire temperature range. The difference between our work and Bux et al.\textsuperscript{15} comes from the difference in the carrier concentrations, while the mobility is almost the same. On the other hand, our work realized larger Seebeck coefficient than the other works because the carrier concentration is lower. The resulting power factor is smaller than those in the previous works although it is comparable to that of Bux et al.\textsuperscript{15} However, this is greatly compensated by the very low thermal conductivity, and as a result, $ZT$ at 850°C of our sample is 25% higher than the best reported value for silicon thermoelectrics using PECVD.\textsuperscript{16,17} In addition, $ZT$ up to 600°C is equivalent to the
best reported value for bulk Si thermoelectrics.\textsuperscript{15} Moreover, the fact that the thermal conductivity is significantly smaller means less material thickness is required to achieve the same temperature gradient, i.e., better cost effectiveness.

VI. SUMMARY

In summary, we have discussed the series of our works that aimed at engineering phonon transport in Si-based nanocrystalline materials, by calculations of multiscale phonon transport in nanocrystalline Si, measurements of thermal boundary conductance at sintered Si–Si interface, and sintering of PECVD Si nanoparticles with controlled oxygen content. Multiscale phonon transport calculations predict effective thermal conductivity of nanocrystalline materials, where the inputs are roughly divided into internal (single crystal) and interfacial (grain boundary) phonon transport properties. The idea pursued here is to obtain the former from first principles calculations and the latter from TDTR measurements of modeled interface. The complementary use of experiment is particularly important to capture diversity and complexity of interfacial structures, which is difficult to deterministically simulate using calculations. The analysis predicts that thermal conductivity of nanocrystalline Si can be greatly suppressed due to the size effect of effective thermal conductivity and large tunability of thermal boundary conductance at the grain boundaries by nano-SiO\textsubscript{2} precipitation. The strategy to control oxygen content has been exercised by actually forming the nanocrystalline Si, which resulted in extremely small thermal conductivity, and thus, large figure of merit. These works should serve as a demonstration of how guidelines to control thermal conductivity can be obtained from physics of phonon transport and be used for actual material development. On the other hand, there remain some ambiguities, such as inconsistency between the modeled planar interface structures and the actual grain boundary structures that are processed at different temperatures, oxide concentrations, and doping concentrations. Together with characterization of interfacial electron transport, these remain to be our future task.

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