I. INTRODUCTION

Direct energy conversion between heat and electricity based on the thermoelectric effects is attractive for its potential applications in the area of waste heat recovery and environmentally-friendly refrigeration. The energy conversion efficiency of a thermoelectric material depends on the dimensionless figure of merit, \( ZT \), which is proportional to the electrical conductivity \( \sigma \), the square of the Seebeck coefficient \( S \), and the absolute temperature \( T \), and inversely proportional to the thermal conductivity \( k \). Recently, the enhancements in \( ZT \) have been achieved using the nanoscale effects, mainly due to the thermal conductivity reduction by phonon boundary scattering at the increased amount of interfaces. Among various methods employing nanostructures, bulk samples with nanoscale grains, which can be treated as a special case of nanocomposites, are one of the most cost efficient ways for large scale application. The process for nanograined materials can be easily scaled up for batch fabrication while maintaining the nanostructures: powders are pulverized into nanometer sizes and consolidated at high temperature. However, experimental results in nanograined SiGe have shown that the porosity can degrade the electrical conductivity so significantly that a high figure of merit cannot be achieved without having a high sample density. Such anomalous reduction in the electrical conductivity cannot be explained by the traditional effective medium theories. Hence, there is a need to better understand the effects of porosity on thermoelectric properties of nanograined materials.

There have been only a few studies on the thermoelectric transport properties of porous media. In the 1970s, Lidorenko et al. reported a 30% increase in the ratio of the electrical conductivity to the thermal conductivity for porous SiGe alloys, and suggested a possible enhancement in \( ZT \) using microscale porous structures. Concurrently, the effective medium theories were exploited to explain the electrical conductivity and the thermal conductivity in such microscale porous materials. However, these studies cannot be applied to nanoscale porous structures due to the classical and/or the quantum size effects: additional scattering of phonons and electrons can happen at the pore sites or at the grain boundaries. More recently experimental and modeling studies on the thermal conductivity of microscale and nanoscale porous films have been made. These studies suggest that the significant reduction in the thermal conductivity of nanoporous structures could lead to the enhancement in \( ZT \). Furthermore, nanoporous structures can also lead to an improvement in the Seebeck coefficient due to the energy filtering effect. Specifically, the Seebeck coefficient can be enhanced by scattering only low-energy electrons when electrons pass through a finite barrier, as previous studies on thermionic emission show.
edge, however, there has been no systematic modeling on how nanoscale porosity affects thermoelectric figure of merit.

This paper presents a modeling study on the effect of nanoscale pores on the thermoelectric properties. First, we investigate why the electrical conductivity of nanoporous materials is degraded more severely than the prediction by the effective medium theories. Second, we explore if the nanoscale porosity effect can lead to the enhancement in ZT. We developed a charge scattering model caused by spherical pore sites to calculate electron transport. For phonon transport, a modified effective medium theory is exploited to consider the classical size effect. Although this model can be applied to various material systems, the result is presented for SiGe, which is widely used as a thermoelectric material for high temperature power generation. The present authors also reported the experimental studies on the nanograined SiGe, which are in line with this modeling study. The modeling results show that the electrical conductivity degradation in nanoporous materials is due to the strong charge carrier scattering at the large number of pore sites. Furthermore, the enhancement in the Seebeck coefficient and the reduction in the phonon thermal conductivity are not large enough to overcome electrical conductivity deterioration in nanoporous SiGe. Hence, this model suggests that a high sample density is essential for the nanograin approach to enhance the ZT of SiGe.

II. MODEL FOR THERMOELECTRIC TRANSPORT IN NANOPOROUS MATERIALS

A. Electron modeling

The electrical conductivity ($\sigma$) and the Seebeck coefficient ($S$) of bulk materials can be derived from the standard formulation based on the Boltzmann transport equation under the relaxation time approximation:

$$ \sigma = -\frac{1}{3} \int q^2 \tau(E) v(E)^2 \frac{\partial f(E_F, E)}{\partial E} D(E) dE, $$

$$ S = \frac{1}{3} \int q \frac{E - E_F}{T} \tau(E) v(E)^2 \frac{\partial f(E_F, E)}{\partial E} D(E) dE/\sigma, $$

where $E$ is the electron energy, $E_F$ is the Fermi level, $q$ is the charge of electrical carriers, $\tau$ is the energy dependent momentum relaxation time, $v$ is the group velocity of the charge carriers, $f$ is the Fermi–Dirac distribution function, and $D$ is the density of electronic states. The validity of this approach relies on the accurate consideration of the momentum relaxation time, or inverse of the scattering rate. In crystalline SiGe, the major scattering mechanisms for electrons are ionized impurity scattering and acoustic phonon scattering. According to the Matthiessen’s rule, when a scattering event happens independently from other scattering events, the total scattering rate is obtained by taking the sum of each scattering rate corresponding to different scattering mechanisms. Functional forms of the momentum relaxation time for various scattering mechanisms can be found in typical device physics textbooks and are summarized in Table 1.

The approach used in this work is similar to that of Vining, but more details are considered. In particular, we consider the nonparabolicity of the conduction band due to a high carrier concentration. The change in band structure with varying temperature and doping concentrations is also considered. The coefficients associated with band structure are taken from the literature as summarized in Table 1.

The validity of our model for dense bulk samples was verified with the experimental results on bulk SiGe alloy by Dismukes et al. While the Fermi level is used as a fitting parameter in Vining’s work, we derived the Fermi level directly from the measured carrier concentration by Dismukes et al. Without using any fitting parameter, our model can fit the experimental data for bulk SiGe alloy for the temperature range of 300 to 1300 K and for the various composition ratios (Fig. 1).

We develop a new scattering model to consider the effect of nanoscale pores on the charge carriers transport properties. Figure 2 shows a schematic of charge carrier scattering caused by a pore site. Pores are regarded as spherical sites with a potential difference. When a charge carrier passes near a spherical pore, it is scattered to a different wave vector due to the potential perturbation. In order to evaluate scattering rate caused by spherical potential, we exploit the Fermi Golden rule as in the other scattering studies. In the scattering rate calculation, it is generally assumed that the band structure is not affected by the potential perturbation. Hence, we neglect any modification in atomic structure caused by the pore sites. The amount of potential perturbation $U_0$ is the difference between the electron energy levels in the pore site and in the environment, and is equivalent to the electron affinity of SiGe. The mathematical form of the spherical scattering potential with a radius $a$ can be expressed as

$$ U(\vec{r}) = U_0 H(a - |\vec{r}|), $$

where $r$ is the distance from the center of pore and $H$ is the Heaviside step function. Using the Fermi’s Golden Rule, we can obtain the transition rate $SR$ from the original eigenstate with the wave vector $\vec{k}$ to another with a wave vector $\vec{k}'$

$$ SR(\vec{k}, \vec{k}') = \frac{2\pi}{\hbar} |M_{\vec{k}\vec{k}'}|^2 \delta(E' - E), $$

where $\hbar$ is Plank’s Constant, $E$ and $E'$ are the energy of charge carriers before and after scattering, and $\delta$ is the delta function. $M_{\vec{k}\vec{k}'}$ is the matrix element of the scattering potential $U$ between the eigenstates $\vec{k}$ and $\vec{k}'$

$$ M_{\vec{k}\vec{k}'} = \int \int e^{i\vec{k}\cdot\vec{r}} U(\vec{r}) e^{-i\vec{k}'\cdot\vec{r}} dx dr dz dz, $$

As the scattering rate measures how often a charge carrier is scattered into a different eigenstate, we need to integrate Eq. (4) over all possible eigenstates $\vec{k}'$ that result from a scattering event. Since we assume that the scattering is elastic, Eq. (4) will have nonzero value only when the energy of charge carriers is conserved. The scattering rate or the inverse of relaxation time, for pore sites is...
The size and the number density of the pores need to be evaluated to calculate the scattering rate in Eq. (7). Once the pore size is known, the number density $N$ can be derived from the definition of the porosity $\Phi$, which is the ratio of the pore volume to the total sample volume

$$N = \frac{3\Phi}{4\pi a^3},$$  \hspace{1cm} (9)

where $a$ is the radius of a spherical pore. In the following paragraph, we will discuss how the pore size is determined.

The pore is regarded as a vacant space among grains. As the grain size becomes smaller, the size of the pore also becomes smaller. To derive the relation between the size of grains and pores, we assume that the grains are closely packed hard spheres with diameter $L$ as shown in Fig. 3. In this case, a space exists inside the four spheres that touch each other. We model the pore site as the sphere that can fit in this space. The pore radius $a$ is derived from the geometry of a tetrahedron as

$$a = \left( \sqrt{\frac{3}{8}} - \frac{1}{2} \right) L. \hspace{1cm} (10)$$

The actual pore radius can be smaller than Eq. (9) due to adhesion forces between grains and the nonspherical geometry of grains.

While additional scattering of charge carriers by pore sites can be determined from Eq. (7), the finite volume of the pores should not be neglected, especially when the porosity...
becomes large. To account for the finite volume of the pores, we treat nanoporous materials as media where one phase is the host material and the other is vacuum. We employ the effective medium theories to calculate the transport properties of the nanoporous media.\textsuperscript{13,14} The effective electrical conductivity and Seebeck coefficient of porous media can be described as

\[ \sigma_{\text{eff}} = \frac{\sigma_h}{2 - 3\Phi}, \]

\[ S_{\text{eff}} = S_h \frac{\gamma_{\text{eff}} \sigma_h}{\gamma_h \sigma_{\text{eff}}}, \]

and \( \gamma \) is defined as

\[ \gamma = k + T\sigma S^2, \]

where \( k \) is the total thermal conductivity. The subscript \( h \) stands for the properties of the host material, which can be calculated from Eqs. (1) and (2) after incorporating the scattering by the pores. Since \( \gamma \) is also dependent on the Seebeck coefficient \( S \), Eq. (12) is solved by numerical iteration. The thermal conductivity used in Eq. (13) includes both the electron and phonon contributions. The electron contribution to the thermal conductivity \( k_e \) can be evaluated from

\[ k_e = -\frac{1}{3} \int \frac{(E - E_F)^2}{T} \sigma(E) v(E)^2 \frac{\partial f(E_F - E)}{\partial E} D(E) dE - S^2 T \sigma. \]

Besides electronic thermal conductivity, phonon contribution to the heat conduction in thermoelectric materials is significant. The transport analysis will not be complete without careful consideration of the change in phonon thermal conductivity of porous nanograin structures. In the following section, the effect of nanosized pores and nanograins on the phonon thermal conductivity is discussed.

B. Phonon modeling

While the Seebeck coefficient and the electrical conductivity are derived by integrating the energy flux and charge flux over all energy levels of electrons, the lattice thermal conductivity is derived by integrating phonon energy flux over all phonon frequencies. The simplified expression of lattice thermal conductivity is

\[ k = \frac{1}{3} \int C(\omega) v(\omega) \Lambda(\omega) d\omega, \]

where \( \omega \) is the phonon frequency, \( C \) is the lattice heat capacity, \( v \) is the sound velocity, and \( \Lambda \) is the phonon mean-free path. The phonon mean-free path is given by the group ve-
where acoustic phonon, i.e., sound velocity, divided by phonon scattering rate. As in the electron transport properties calculation, we consider the various scattering mechanisms to determine the phonon scattering rate. Three-phonon scattering, point defect scattering, and phonon-electron scattering are the major scattering mechanisms for phonons in the bulk SiGe alloy. The functional forms of each scattering rate and the required constants are listed in Table II. Each scattering rates calculated by the different scattering mechanisms is superposed using Mathiessen’s Rule. In addition to these scattering mechanisms in bulk SiGe, phonons will be scattered diffusively at grain boundaries. When the grain size is smaller than the bulk phonon mean-free path, the grain boundary scattering becomes dominant. In this case, the effective phonon mean-free path will be limited by the small grain size $L$ and given by:

$$\frac{1}{\Lambda_{\text{effective}}} = \frac{1}{\Lambda_{\text{bulk}}} + \frac{1}{L}.$$  \hfill (16)

The actual functional forms for the lattice thermal conductivity are slightly more complicated than Eq. (15) and are taken from studies in the 1960s (Table II) (Refs. 32 and 33).

For the lattice thermal conductivity in porous structures, we use the modified formulation of the effective medium theory. A simplified expression for the lattice thermal conductivity of porous media is described as follows:

$$k_{\text{eff}} = k_b \frac{2 - 2\Phi}{2 + \Phi},$$  \hfill (17)

where $k_{\text{eff}}$ is the effective thermal conductivity, $k_b$ is the thermal conductivity of the host, and $\Phi$ is the porosity. The effect of small grain size is taken into consideration for the host thermal conductivity calculation, using Eqs. (15) and (16). By this way, the modified effective medium theory considers both the classical size effect and the porosity effect on the lattice thermal conductivity.

### III. RESULTS AND DISCUSSIONS

Figure 4 shows our modeling results fitted on the experimental data reported by Lidorenko. Due to lack of information on grain size and carrier concentration, we take them as fitting parameters. We use a grain size of 10 $\mu$m and concentration of 10$^{20}$/cm$^3$, to match the trends of both the thermal conductivity and the electrical conductivity. For the 10 $\mu$m pores, electrons are not significantly scattered by the pores due to the large separation between pores. Since the screening length of charge carriers in the solid portion is 1 nm order of magnitude, the sparse pore sites will not affect the charge carrier transport. Therefore, the reduction in the electrical conductivity is mainly attributed to the lack of medium. However, when the grain size is on the nanometer scale, the interpore spacing becomes shorter, and electron transport is severely limited by the scattering from the pores.

Figure 5 shows the energy dependency of charge carrier scattering by the spherical potential model for 20 nm grain size with 1% porosity. The energy dependent scattering rate provides the logical bases for low electrical conductivity and enhanced Seebeck coefficient. At this pore size and porosity, the pore scattering dominates the total momentum relaxation time. Without the scattering by the pores, the momentum relaxation time is an order of magnitude higher, which indicates that the electrical conductivity decreases significantly by the nanosized pores. However, the pore scattering can provide us with an advantage of the enhanced Seebeck coefficient, which results from the more efficient scattering of low-energy electrons than high-energy electrons. Conse-
quently, the Seebeck coefficient, which measures an average energy of electrons that contribute to electrical conductivity, is enhanced by reducing the contributions from low-energy electrons.

Figures 6 and 7 show the thermoelectric properties for the porosity range between 0% and 15% and for grain sizes down to 20 nm. The 20 nm is the grain size that we observed for SiGe nanograined samples with a high ZT.\textsuperscript{22,23} In the calculations, we use a temperature of 1300 K and a doping concentration of $1.5 \times 10^{20} / \text{cm}^3$ that is typical for high temperature SiGe thermoelectric power generation. As demonstrated in Figs. 6(b) and 7(b), the enhancement in the Seebeck coefficient due to the nanoscale pores becomes larger for smaller grain size. However, the momentum relaxation time of the porous materials is much smaller than that of materials with high sample density (Fig. 5), so that the electrical conductivity of the nanoscale porous media is severely degraded compared to their bulk counterparts [Figs. 6(a) and 7(a)]. Figure 7(a) also shows that the electrical conductivity is degraded more as the grain size decreases with the porosity kept constant. While the scattering rate is roughly proportional to the square of the pore size as shown in Eq. (7),
number density is inversely proportional to the third power of the pore size, so that the scattering rate is higher for smaller grain size. When the grain size gets as small as 20 nm and the porosity gets larger than 10%, the strong scattering due to porosity is not even favorable to the Seebeck coefficient [Fig. 6(b)].

The thermal conductivity also decreases as the grain size is reduced [Fig. 7(c)]. In the limit of no porosity, this trend can be explained by the classical size effect that reduces the phonon contribution to the thermal conductivity. When the porosity is not negligible, the electron contribution to the thermal conductivity is also reduced by strong scattering at the nanoscale pore sites. Although the electron contribution is often considered to be small in SiGe, it becomes comparable to that of phonons in nanograined SiGe due to significant reduction in the phonon contribution. As a consequence, the total thermal conductivity reduction is larger for smaller grain size and higher porosity [Figs. 6(c) and 7(c)].

In spite of the reduction in the thermal conductivity and the enhancement in the Seebeck coefficient, the porous nanograined SiGe cannot lead to a high ZT because the electrical conductivity drops so significantly due to porosity is not even favorable to the Seebeck coefficient, the electrical conductivity drops so significantly that the porosity degrades the thermoelectric figure of merit in nanograined SiGe. Hence, a high sample density is required to achieve a net ZT enhancement in nanograined SiGe. However, an enhancement in ZT by the porosity effect may be observed in other material systems. For example, materials with small electron effective mass and a low relaxation time of charge carriers would exhibit a smaller reduction in the electrical conductivity than for SiGe. The present model can be used to find such materials and calls for further studies on such potential candidate materials.

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