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Pore-size dependence of the thermal conductivity of porous silicon: A phonon hydrodynamic approach

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Phonon hydrodynamics is used to analyze the influence of porosity and of pore size on reduction in thermal conductivity in porous silicon, with respect to crystalline silicon. The expressions predict that the thermal conductivity is lower for higher porosity and for smaller pore radius, as a consequence of phonon ballistic effects. The theoretical results describe experimental data better than the assumption that they only depend on porosity. © 2010 American Institute of Physics. [doi:10.1063/1.3462936]

The thermal conductivity of porous silicon has been found to decrease greatly for increasing porosity, getting two or three orders of magnitude lower than for monocrystalline silicon.^{1–11} These low thermal conductivity values allow us to use this promising material as thermal insulator in microsensors and microsystems. Furthermore, optimization of its use in optoelectronic applications, due to its outstanding photoluminescence properties, requires a good knowledge of its thermal properties. Because of these applications, this topic has become of much interest in nanoscale heat transport.^{12–14} Often this problem is treated from kinetic theory for phonons, or from molecular simulations⁷ but here we study it from a more thermodynamic perspective. We propose to apply phonon hydrodynamics^{15–19} to the analysis of the thermal conductivity of porous silicon, considered as a solid matrix with a random inclusion of small insulating spheres. Our aim is to explore the influence of the pore size on the effective thermal conductivity λ_{eff} . In the simplest theoretical models, the thermal conductivity depends only on the porosity ϕ , the volume fraction corresponding to the pores, with $\lambda_{\text{eff}} = f(\phi)k_0$, $f(\phi)$ being a function smaller than 1, as for instance $f(\phi) = (1 - \phi)^3$.² However, experimental results show that the pore size also plays a relevant role in the reduction in thermal conductivity.^{2,11} A detailed knowledge of this dependence may have valuable practical consequences. Since increasing porosity also deteriorates the electron transport properties,^{20,21} being able to reduce thermal conductivity by several alternative procedures opens a wider range of possibilities, which may be of interest in thermoelectric applications.

In a series of papers^{22–24} we have used phonon hydrodynamics to describe heat transfer along nanowires and thin layers, taking into account boundary conditions describing the phonon-wall interactions. In contrast with Fourier's law, this approach incorporates nonlocal effects dependent on the ratio of the mean free path ℓ to the characteristic size of the system a , the so-called Knudsen number $\text{Kn} \equiv \ell/a$, and provides a much simpler approach to a quantitative expression

for the thermal conductivity than solving the full Boltzmann transport equation.

When the mean free path becomes comparable or longer to size of the system, the classical Fourier equation for heat transport is no longer valid and nonlocal effects must be incorporated. Here, we start from the Guyer–Krumhansl equation for the heat flux, as follows:^{15–19}

$$\tau \frac{d\mathbf{q}}{dt} + \mathbf{q} = -\lambda_0 \nabla T + \ell^2 [\nabla^2 \mathbf{q} + 2 \nabla (\nabla \cdot \mathbf{q})], \quad (1)$$

where \mathbf{q} is the heat flux, ℓ the mean free path of the phonons, λ_0 the bulk thermal conductivity, and τ the relaxation time of the heat flux.

This equation has been widely studied for porous media.^{25–28} However, since we will be working in situations for which the radius of the obstacles is less than the mean free path, we will also consider slip boundary conditions over the surface of the obstacles, which is found when one considers the flow of rarefied gases.^{29–31} In our case, we take for the characteristic size a the radius of the pores.

For steady situations, when the first and the last term in (1) are zero, and in situations where the spatial variation in the heat flux is higher than the heat flux itself, namely, in the high-Knudsen regime, the term in \mathbf{q} in (1) may be also neglected, and (1) reduces to $\lambda_0 \nabla T = \ell^2 \nabla^2 \mathbf{q}$. This equation is analogous to the Navier–Stokes equations for Poiseuille flow, and it may also be used for Stokes problem for small Reynolds number, when nonlinear terms in the time derivative of the velocity are negligible. In this case, ∇T plays the role of the pressure gradient, ∇p , and ℓ^2/λ_0 the role of the viscosity. In Refs. 22–24 we have applied it to nanowires, taking into account suitable boundary conditions for the heat flux on the walls. For small values of the heat flux, this equation may be applied to describe the phonon heat flux around an insulating sphere. Thus, we may translate from results of fluid dynamics to the description of heat transfer in these circumstances.

First, we recall some results of fluid dynamics necessary for our problem. In the presence of a sphere of radius a in an infinite medium, the resistance force is given by the Stokes formula $F = 6\pi\eta av$, where η is the shear viscosity of the fluid and v the relative velocity of the sphere with respect to the fluid. For rarefied flows, the tangential velocity (or slip

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flow) on the surface of the sphere must also be taken into account. For high Knudsen numbers, the expression are very complicated but we may use a generalization of the Stokes law to arbitrary Knudsen numbers, given by³²

$$F = \frac{6\pi\eta a}{1 + A'(\ell/a)}v, \quad (2)$$

where A' is a numerical function of Kn which varies from 0.700 for small Kn to 1.164 for large Kn. This expression describes the transition from the diffusive limit (Kn=0) for which $F \propto a$ to the highly ballistic limit (high Kn) where $F \propto a^2$. Millikan³² proposed for A' the heuristic form $A' = A_1 + B_1 \exp(-\gamma a/\ell)$, with $A_1 = 0.864$, $B_1 = 0.290$, and $\gamma = 1.25$. Other proposals have been done^{33,34} but here this one will be sufficient for our purposes. In particular, an asymptotic expansion of a hierarchy of higher-order equations including (1) as the first term allows to describe the diffusive-to-ballistic transition, leading to analogous asymptotic behaviors as (2) (Ref. 35) but here it is not necessary to go to so many details.

Since in our problem there is not a single sphere but an array of spheres, and since the effects of the several spheres are not simply additive, the calculation of the effects is very complicated but it has been explored in the literature.^{25-27,36} We assume a random array of spheres and use the result by Brinkman²⁵

$$F = \frac{6\pi\eta a}{1 + A'(\ell/a)} \left(1 + \frac{3}{\sqrt{2}} \sqrt{\phi} \right) v, \quad (3)$$

where ϕ is the porosity, i.e., the volume fraction of spheres $\phi = (4\pi/3)N(a/L)^3$, L being the separation of the centers of the spheres. This gives the influence of other spheres on the force on a given sphere.

We may now apply the results (2) and (3) to phonon hydrodynamics, taking into account the parallelism presented above between pressure gradient and temperature gradient and between shear viscosity and ℓ^2/λ_0 . The contribution of N randomly distributed spheres to the thermal resistance may be written as

$$F_N = 6\pi N \frac{\ell^2}{\lambda_0} \frac{a}{1 + A'(\ell/a)} \left(1 + \frac{3}{\sqrt{2}} \sqrt{\phi} \right) Q = A \nabla T, \quad (4)$$

where Q is heat flow, A the transversal area of the system (perpendicular to the direction set by the temperature gradient) and F_N the total “resistance force” exerted by the spheres on the phonon flow, which must be equated to the “driving force” of the temperature difference. This “resistance” of the spheres must be added to the normal resistance of heat transport in the medium, which will be $A \nabla T = [f(\phi)\lambda_0]^{-1}Q$, $f(\phi)$ being a function which describes the geometrical effects of the porosity in reducing the effective thermal conductivity, as mentioned in the introduction. Dividing both terms in (4) by the volume AL' of the system, with L' the distance between the opposite boundaries of the system in the direction of the temperature gradient, expressing N in terms of the porosity ϕ , and adding the normal diffusive resistance, we obtain for the effective thermal conductivity of the porous medium

TABLE I. Experimental data on the thermal conductivity of amorphous Si for different porosities and pore radii, and theoretical results obtained from Eqs. (5) and (7). In the first column it is indicated the corresponding bibliographical reference.

Case	Porosity (%)	Radius (nm)	Experimental (W m ⁻¹ K ⁻¹)	Equation (5) (W m ⁻¹ K ⁻¹)	Standard [Eq. (7)] (W m ⁻¹ K ⁻¹)
1 ^a	40	1–5	1.2	1.0–4.6	32
2 ^c	40	100	31.2	29.6	32
3 ^c	50	10	3.9	5.9	18.5
4 ^c	60	10	2–5	4.0	9.5
5 ^b	64	2	0.20	0.29	0.35
6 ^b	71	2	0.14	0.16	0.18
7 ^b	79	3	0.06	0.10	0.10
8 ^b	89	5	0.04	0.02	0.02

^aReference 1.

^bReference 2.

^cReference 3.

$$\lambda_{\text{eff}} = \lambda_0 \frac{1}{\frac{1}{f(\phi)} + \frac{9}{2} \phi \frac{(\ell/a)^2}{1 + A'(\ell/a)} \left(1 + \frac{3}{\sqrt{2}} \sqrt{\phi} \right)}. \quad (5)$$

For small mean free path $\ell \ll a$ this reduces to $\lambda_{\text{eff}} = f(\phi)\lambda_0$, whereas the second term in the denominator describes the role of the pore size. For the sake of comparison with experimental data we take, following Ref. 2, $f(\phi) = (1 - \phi)^3$. This comes from a model^{37,38} in which $\lambda_{\text{eff}} = (1 - \phi)g\lambda_0$, where g is the percolation strength, which is related to the fraction of the solid phase which is topologically interconnected and that contributes to the conductivity. This factor is often approximated as $g = (1 - \phi)^2$;

In,⁷ Lee *et al.* have also studied the influence of the pore size on the effective thermal conductivity, taking into account the ballistic character of phonon transport. They derived from kinetic theory for a two-dimensional system with cylindrical transverse pores of radius a that

$$\lambda_{\text{eff}} = \lambda_0 \frac{1}{\frac{1}{f(\phi)} + \alpha \frac{\sqrt{\phi}}{F(\phi) a}}, \quad (6)$$

with the constant $\alpha = 25.5$ and the functions being $f(\phi) = (1 - \phi)/(1 + 1821.1\phi^{1.9})$ and $F(\phi) = (4\phi/\pi)^{1/2} \{ \sin^{-1}[(4\phi/\pi)^{1/2}] - \pi/2 \} + [1 - (4\phi/\pi)]^{1/2}$. According to Ref. 7, $f(\phi)$ accounts for the phonon diffusion in the reduced space left by the porosity, and $F(\phi)$ for the ballistic character of the phonons. Note that in the denominator of (6) the influence of the pore size takes the form $1/a$, as well as in the denominator of (5) for high values of the Knudsen number. However, Eq. (5) is valid for three-dimensional systems and it gives not only the extreme ballistic phonon influence on the pores but also their influence in the diffusive-to-ballistic transition.

Now, we compare the results obtained from (5) and from the simple proposal²

$$\lambda_{\text{eff}} = \lambda_0 (1 - \phi)^3, \quad (7)$$

with experimental results. In the Table I we list several data for the thermal conductivity of porous Si at several porosities and with different pore radii at $T = 300$ K, obtained by different methods. We recall that at this temperature $\lambda_0 = 148$ W m⁻¹ K⁻¹ and $\ell = 40$ nm

The four first values (obtained from Refs. 1 and 3) correspond to crystalline Si with pores, whereas the other four results (from Ref. 2) correspond to porous polycrystalline silicon. In this case, the size of the individual crystallites is that indicated as pore size in the Table because we have assumed that the size of the pores is of the same order as that of crystallites. The difference between the bulk thermal conductivity of crystalline Si and of polycrystalline Si is dramatic, because the mean free path (40 nm in crystalline Si) becomes of the order of the crystallite sizes in the second material, thus leading to a drastic shortening of it and, consequently, to a strong reduction in the bulk material, even in the absence of pores. The reduction is given by the ratio of the crystallite size to the mean free path in crystalline Si, namely $\lambda_{0,\text{pol}} = \lambda_0(d/\ell)$. Consistently with this fact, in these cases we have taken in (5) for the bulk thermal conductivity of the Si matrix the values 7.4 (experiments 5 and 6), 11.1 (experiment 7) and 18.5 (experiment 7), and for the mean free path the crystallite size (i.e., in cases 5–8 we have taken $\ell/a=1$, because both the mean free path and pore size have been assumed to have the same value).

In the last two columns we list the values obtained from Eq. (5) and those from (7). Comparing cases 1 and 2, corresponding to the same porosity, it is clearly seen that the pore radius may be very influential. In general, the results of Eq. (5) are closer to the experimental values because they incorporate the influence of the pore size which, according to (5) contribute to a reduction in the conductivity.

It follows from (5) that thermal conductivity not only depends on the porosity but also on the pore size, leading to thermal conductivities lower than those expected by porosity when the factor ℓ/a is relevant. Small-pore samples have smaller thermal conductivity compared to large pores, at equal porosity values because for the same mean free path the ratio ℓ/a in the denominator is bigger for the smaller radius. In microscopic terms, the reduction in the thermal conductivity of smaller pore radius may be interpreted as increased phonon scattering at the pore surfaces.⁷

The effect of an inclusion of spheres of radius a and thermal conductivity λ_2 inside a matrix of a material of thermal conductivity λ_1 is a classical problem that was already studied by Lord Rayleigh in 1892 (see Ref. 39 for references). The interest in nanosystems has pushed these topics to the consideration of very small scales, where the pore size and the separation between pores is comparable of smaller than the mean free path, where the effect of the reduction is much stronger.

In summary, phonon hydrodynamics, complemented with classical hydrodynamic results for rarefied flows in porous media, provides a phenomenological way to describe the effects of the pore size on the thermal conductivity reduction, which may be rather strong. Combining the two parameters porosity and pore size, would allow more possibilities to optimize some material functions of the porous Si.

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