How embedding nanoparticles effects semiconductor thermal conductivity

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Abstract: In this paper we study how the thermal conductivity of semiconductors is effected by embedding in them nanoparticles, which act as extrinsic phonon scattering centers. The study is based on a new formula for thermal conductivity, which has recently been found on the basis of Extended Thermodynamics. All the other main interactions of phonons among themselves, with isotopes and boundaries are taken into account. Numerical results are shown for the case of germanium nanoparticles embedded in a Si$_{0.7}$Ge$_{0.3}$ alloy crystal.

Key–Words: Thermal conductivity, Nanoparticles, Maximum Entropy Principle

1 Introduction

Heat conduction in semiconductors and insulators is a very important issue [4, 5, 6, 10, 12, 14, 15]. In particular, reducing thermal conductivity is crucial in order to improve the efficiency of solid-state thermoelectric converters and make them competitive with the traditional electric generators or refrigerators. The efficiency of a thermoelectric converter is determined by the dimensionless figure of merit $ZT = \frac{\sigma S^2}{\kappa T}$, where $Z$ is the figure of merit, $T$ the absolute temperature, $\sigma$ the electrical conductivity, $S$ the Seebeck coefficient, and $\kappa$ the thermal conductivity. One of the most effective methods to obtain such a reduction is that of embedding nanoparticles in alloy crystals such as InGaAs or SiGe [5, 10]. This is a problem far from being simple, since it is necessary to find particles that be grown into the alloy without creating dislocations [10]. In [5] a formula for thermal conductivity, obtained by solving the Boltzmann-Peierls acoustic phonon transport equation in the frequency domain, is used to analyze the effect of embedding spherical Ge nanoparticles in a Si$_{0.7}$Ge$_{0.3}$ alloy crystal matrix. It is shown that, as a consequence, the steady-state thermal conductivity is reduced, while the cut-off frequency $f_C$ of the dynamical conductivity is increased with respect to the intrinsic alloy. Both these effects could be very advantageous in many micro-electronic and optoelectronic device applications. In this paper, we will apply a recent formula for thermal conductivity in order to confirm the previous results. The formula has been obtained by means of a hierarchy of macroscopic models. The variables used to describe the state of the acoustic phonons, to which heat transport in semiconductors is mainly due, are moments of their occupation numbers. The models can be considered as a generalization of the Cattaneo equation, which was introduced to circumvent the deficiencies of Fourier law in describing processes involving high heating rates. The evolution equations for the moments have been found by integration from the Boltzmann-Peierls equation and they are closed on the basis of the Maximum Entropy Principle (MEP). Exploiting these equations, we show that it is possible to obtain a correct description of thermal conductivity in presence of nanoparticles, if a suitable set of moments is chosen.

2 The macroscopic model and the new formula for thermal conductivity

In dielectric materials, energy is essentially carried by phonons, which approximately behave like quasiparticles that obey Bose statistics. In particular, since the group velocity of the optical phonons is nearly zero, it can be assumed that heat is carried only by longitudinal and transverse acoustic phonons (LA and TA respectively). The kinetic description is based on the occupation number of phonons $g_p(x, t, q), p = \text{LA, TA}$, which is a function of the space vector $x$, the time $t$, the phonon wave vector $q$ and polarization $p = \text{LA, TA}$. Its time evolution is governed by the
Boltzmann-Peierls equation

\[ \frac{\partial g_p}{\partial t} + v_p \cdot \nabla_x g_p = C_p(g_p), \quad p = LA, TA, (1) \]

where \( v_p, p = LA, TA, \) is the group velocity and the collision operators \( C_p, p = LA, TA, \) describe interactions of phonons among themselves (umklapp and normal anharmonic processes) and with lattice imperfections, as well as with the boundaries of the crystal. For the collision operators, the Callaway relaxation time approximation [2, 4, 7] is commonly used. In [4], by solving equation (1) in the frequency domain under suitable hypotheses, the following formula for the dynamical thermal conductivity is obtained

\[ \kappa(\Omega) = \kappa_r(\Omega) + i\kappa_i(\Omega), \quad (2) \]

with the real and imaginary parts of the lattice conductivity respectively given by

\[ \kappa_r(\Omega) = \sum_p C_p T^3 \int_0^{\theta_p^D/T} \frac{\phi_p^T}{1 + (\Omega \tau_p^C(x))^2} d\Omega, \]

\[ \kappa_i(\Omega) = \sum_p C_p T^3 \int_0^{\theta_p^D/T} \frac{\omega_p \tau_p^{eff}(x) D(x)}{1 + (\Omega \tau_p^{eff}(x))^2} d\Omega, \]

where \( \Omega \) is the circular frequency, \( \theta_p^D \) the Debye temperature [12] of the acoustic polarization branch \( p = LA, TA, \)
\( D(x) := \frac{e^{\theta_p^D x}}{(e^{\theta_p^D} - 1)^2}, \quad C_p = \frac{4 \pi m_p k_B^2}{3 \theta_p^D}, \)
with \( k_B \) the Boltzmann constant and \( g_p, p = LA, TA, \) the phonon density of states. The combined and the effective total relaxation times, \( \tau_p^C \) and \( \tau_p^{eff} \), are respectively given by

\[ \frac{1}{\tau_p^C} := \frac{1}{\tau_p^R} + \frac{1}{\tau_p^N}, \quad \tau_p^{eff} := \left( 1 + \frac{\beta_p}{\tau_p^N} \right) \tau_p^C, \]

with \( \tau_p^R \) the resistive relaxation time, whose reciprocal, on its turn, is the sum of the reciprocal umklapp, impurity and boundary relaxation times (the processes relative to these relaxation times are said resistive since they do not conserve the total momentum), \( \tau_p^N \) the normal relaxation time (the relative process does conserve the total momentum), and \( \beta_p \) the Callaway parameter [2, 4, 7]. For the explicit expressions of the above-mentioned relaxation times as functions of the temperature and the phonon energy \( \epsilon_p \), we refer the reader to [12]. Here, we specify only the reciprocal relaxation time of the scattering process generated by the presence of nanoparticles, which, has to be added to the reciprocal relaxation times of the other resistive processes, since the latter process does not conserve the total momentum either. In the linear regime, by assuming a spherical shape of the nanoparticles and using a Mathiessen type interpolation between the long and the short wavelength scattering regimes, it is given by

\[ \frac{1}{\tau_p^{np}} = v_p (\sigma_{ps}^{-1} + \sigma_{pl}^{-1})^{-1}, \quad (3) \]

where \( v_p := |v_p|, \quad V_{np} = \frac{\pi}{12} \pi R^3 \) is the volume of a nanoparticle of radius \( R, \sigma_{ps} \) and \( \sigma_{pl} \) are the short and long wavelength cross sections, which are respectively given by

\[ \sigma_{ps} = 2 \pi R^2, \quad \sigma_{pl} = \frac{4 \pi}{9} \left( \frac{\rho - \rho_{np}}{\rho} \right) \frac{\pi R^6}{\hbar v_p} \left( \frac{\epsilon_p}{\hbar v_p} \right)^4, \]

with \( \rho \) the density of the host matrix material, \( \rho_{np} \) that of the embedded nanoparticles, \( \hbar \) the reduced Planck constant, and \( f_{np} \), the nanoparticle volume fraction. Starting from the Boltzmann-Peierls equation, it is possible to derive macroscopic models by using the moment method. In particular, we will consider the following weight functions of the acoustic phonon wave vector \( \{ \psi_p(q) \} := \{ \epsilon_p, v_p, \epsilon_p^{1/s_1} v_p, \epsilon_p^{2/s_1} v_p, ... , \epsilon_p^{s_1} v_p, \epsilon_p^{1/s_2} v_p, ... , \epsilon_p^{1/s_2} v_p, \epsilon_p^{1-s_2/2} v_p \}, \) with \( s_1, s_2, M \in \mathbb{N} \) fixed, to which the below written moments of the occupation number there correspond:

\[ W_p = \int_B \epsilon_p g_p dq, \]

\[ Q_p^M = \begin{cases} \int_B \epsilon_p^{(M-1)/s_1} v_p g_p dq, & M = 1, \ldots, s_1 + 1, \\ \int_B \epsilon_p^{1+(M-s_1-1)/s_2} v_p g_p dq, & M = s_1 + 2, \ldots, M + s_1 + 1, \end{cases} \quad (4) \]

where \( B \) is the first Brillouin zone, \( W_p \) are the phonon average energies and \( Q_p := Q_p^{s_1+1}, p = LA, TA, \) the heat fluxes, while the other moments do not have an immediate physical interpretation. Other choices of moments are possible [7, 8], depending on the physical situation one needs to describe. The results will show that the previous one is very suitable to the description of thermal conductivity. The evolution equations for the chosen state variables can be derived directly from the Boltzmann-Peierls equation by integration:

\[ \frac{\partial}{\partial t} \left( \frac{W_p}{Q_p^M} \right) + \nabla_x \cdot \left( \frac{Q_p^M}{T_p} \right) = \left( \frac{C_{W_p}}{C_{Q_p}} \right), \quad (5) \]

\[ M = 1, 2, \ldots, M + s_1 + 1. \quad (6) \]
In the above equations, there appear the following extra-fluxes and production terms

\[
\begin{align*}
\mathbf{T}^M_p &= \begin{cases}
\int_{B} \varepsilon_p^{(M-1)/s_1} \mathbf{v}_p \otimes \mathbf{v}_p d\mathbf{q}, & M = 1, \ldots, s_1 + 1, \\
\int_{B} \varepsilon_p^{1+(M-s_1-1)/s_2} \mathbf{v}_p \otimes \mathbf{v}_p d\mathbf{q}, & M = s_1 + 2, \ldots, M + s_1 + 1,
\end{cases}
\end{align*}
\]

\[
C_{W_p} = \int \varepsilon_p C_p(g_p) d\mathbf{q},
\]

\[
C_{Q_p} = \begin{cases}
\int_{B} \varepsilon_p^{(M-1)/s_1} \mathbf{v}_p C_p(g_p) d\mathbf{q}, & M = 1, \ldots, s_1 + 1, \\
\int_{B} \varepsilon_p^{1+(M-s_1-1)/s_2} \mathbf{v}_p C_p(g_p) d\mathbf{q}, & M = s_1 + 2, \ldots, M + s_1 + 1.
\end{cases}
\]

The quantities \(T_p^{s_1+1}, C_{W_p}, C_{Q_p}^{s_1+1}, p = LA, TA\), respectively are the flux of the heat flux, and the energy and heat flux productions, while the remaining extra-fluxes and production terms do not have an immediate physical interpretation.

Therefore, in the evolution equations the number of the unknowns is greater than that of the equations, which means that constitutive equations are needed for the extra-variables. A systematic and successful way to get these constitutive equations is based on the MEP [1, 3, 9, 11, 13], which furnishes the following relations (interested are referred to [7] and references therein for details)

\[
\mathbf{T}^M_p = \frac{4}{3\pi y_p} \left( k_BT \right)^{M+3} \left( \frac{h^3 v_p}{\eta} \right) K_{M+2}^p(T) \mathbf{I}_3,
\]

with \(\mathbf{I}_3\) the identity tensor of rank 3, and

\[
K_{M}^p(T) := \int_0^{\theta_p^D/T} \frac{x^M}{e^x - 1} dx,
\]

\[
C_{W_p} = 0,
\]

\[
C_{Q_p} = \sum_{\eta, KL} q_{MK}^{(p,n)} k_p Q_p^L, p = LA, TA,
\]

where \(\eta = U, N, B, I, n_p\), labels the umklapp, normal, boundary, impurity and nanoparticle scattering processes,

\[
q_{MK}^{(p,N)}(T) = \frac{4\pi y_p}{3h^3 v_p} (k_BT)^{M+3} J_{M+K+2}^{(p,N)} - J_{M+3}^{(p,N)} J_{M+K+3}^{(p,N)},
\]

\[
q_{MK}^{(p,\alpha)}(T) = \frac{4\pi y_p}{3h^3 v_p} (k_BT)^{M+3} J_{M+K+2}^{(p,\alpha)},
\]

\[
\alpha = U, B, I, np,
\]

with

\[
J_{M}^p(T) := \int_0^{\theta_p^D/T} \frac{x^M e^x}{\mathbf{T}_p(x)(e^x - 1)^2} dx,
\]

and the \(b_{MK}^p\)'s are the elements of the inverse of the matrix \(a_{MK}^p\) with elements

\[
a_{MK}^p(T) := -\frac{4}{3\pi y_p} \left( \frac{h^3 v_p}{\eta} \right) J_{M+K+2}^p,
\]

and

\[
J_{M}^p(T) := \int_0^{\theta_p^D/T} \frac{x^M e^x}{(e^x - 1)^2} dx.
\]

Using these relations, equations (6) can be put in the following form

\[
\frac{\partial}{\partial T} Q_p^M + F_p^M \nabla_x T = \sum_{K,L} b_{MK}^{p} Q_p^{K}, \quad (7)
\]

\[
T = 1, 2, \ldots, M + s_1 + 1,
\]

where

\[
F_p^M(T) := \frac{4\pi y_p}{3h^3 v_p} \int_0^{\theta_p^D/T} \left( k_BT \right)^{M+3} K_{M+2}^p(T)
\]

Under the hypothesis, analogous to that assumed in [4], that the time variation of the \(F_p^M, q_{ML}^p, b_{ML}^p\), \(L, M = 1, \ldots, M, p = LA, TA\), is negligible, if we take the Fourier transforms of (7) and solve them with respect to the Fourier transforms of the fluxes \(Q_p^M\), we obtain

\[
\left( \mathbf{Q}_p^M \right)_i = \sum_{L} \left( \mathbf{Q}_p^M B^p + i\Omega T_M \right)^{-1} [M]_{p}^{L} F_p^L \frac{\partial T}{\partial x_i},
\]

\[
i = 1, 2, 3, \quad M = 1, 2, \ldots, M + s_1 + 1,
\]

with \(\mathbf{Q}_p^M(T)\) and \(B^p(T)\) the matrices of elements \(\sum_{\eta} q_{ML}^{(p,n)}\) and \(b_{ML}^p\) respectively, and \(T_M\) the identity
tensor of rank $M + s_1 + 1$. We notice that for $M = s_1$, the relation between the Fourier transform of the heat flux and the Fourier transform of the temperature gradient is retrieved, and therefore the following expression for the dynamical thermal conductivity holds

$$\kappa(\Omega) = \sum_{p,M} \left( i\Omega T_M + (Q^p B^p) \right)^{-1}_{s_1+1,M} F_p^M$$

$$= - \sum_{p,L,M} (\Omega^2 T_M + (Q^p B^p)^2)_{s_1+1,L} (Q^p B^p)_{LM} F_p^M$$

$$+ i\Omega \sum_{p,M} (\Omega^2 T_M + (Q^p B^p)^2)^{-1}_{s_1+1,M} F_p^M . (8)$$

From the latter expression it is clear that the real and imaginary parts of $\kappa(\Omega)$ are the Hilbert transforms of each other. Therefore the causality requirement is fulfilled, for which the temperature gradient is the cause and the heat flux the effect [4].

3 Application to Si$_{0.7}$Ge$_{0.3}$

In this section we will apply the previous formula for thermal conductivity in order to study the effect of embedding spherical Ge nanoparticles in a Si$_{0.7}$Ge$_{0.3}$ matrix. If nanoparticle volume fractions up to 10% and nanoparticles of radii in the range going from 1 to 100 nm are considered, their influence on the electron mobility can be neglected [5, 10]. Furthermore it will be assumed that the nanoparticles do not affect the intrinsic physical properties of the semiconductor host alloy, which can be found in tables I and II of [4]. We start considering the steady-state thermal conductivity $\kappa(0)$ for a nanoparticle fraction $f_{np} = 2\%$, which is obtained from (8) for $\Omega = 0$. In Fig.1 we represent the behaviour of $\kappa(0)$ as a function of temperature for different values of the radius of the embedded nanoparticles, compared with the case when no nanoparticles are present. It can be seen that the thermal conductivity decreases at the increasing of the radius and its peak shifts to the right. As already noted in [5] the effect is more evident at low temperatures, where the thermal conductivity continues to decrease at increasing values of $R$, while it tends to saturate at high temperatures. Moreover, at low temperatures $\kappa(0)$ does not follow the $T^3$ power law of the specific heat, which is typical of the case with no nanoparticles.

In Figs. 2 and 3, the steady-state thermal conductivity is reproduced as a function of the nanoparticle radius for the temperatures $T = 3, 20, 300, 500, 1000$K. It can be seen that for any value of the temperature there is a value $R_{min}$ of $R$ at which the thermal conductivity reaches a minimum value, and that $R_{min}$ diminishes at the increase of $T$ (for $T = 1000$K it is out of the considered range of values of $R$). This is a feature already highlighted in [10] and [5], and due to the interplay between the long and short wavelength scattering regimes, see equation (3). Figs. 2 and 3 also confirm that the effect of embedding nanoparticles on conductivity is smaller at higher temperatures. As regards the dynamical thermal conductivity, we consider two values of the temperature, $T = 3$K and $T = 300$K.

For the first value, in Figs.4 and 5 we report the behavior of the amplitude of the dynamical conductivity as function of the frequency $f = \Omega/2\pi$ and for $R = 1, 3, 5, 7, 10$nm. The main difference with re-
Steady-state thermal conductivity (W/cm K) vs Nanoparticle radius (nm) for $T=300, 500, 1000$K.

Figure 3: Steady-state thermal conductivity vs $R$, for $f_{np} = 0\%, 2\%$ and $T = 300, 500, 1000$K.

Amplitude of the dynamical thermal conductivity (W/cm K) vs Frequency (Hz) for $T=300$K. 

Figure 4: Amplitude of the dynamical thermal conductivity vs $f$, for $f_{np} = 0\%, 2\%$, $T = 3$K and $R = 1, 3$ nm.

is greater in the case of embedded nanoparticles, in fact in Figs.4 and 5 the intersection between the curve representing the amplitude and $\kappa = \kappa_C$ is at higher $f$ at the increase of $R$. In Figs.6 and 7 analogous results are presented for the case $T = 300$K.

We conclude with some considerations about the choice of the moments. Fractional powers of the energy have been used in the weight functions of the vector moments, since the corresponding matrices $\mathcal{B}$ and $\mathcal{Q}$ result better conditioned and convergence is faster.

In particular, we have taken $s_1 = 4$, $s_2 = 3$ or 4 (according to the values of $T$ and $R$) and $\bar{M} = 5$.

Figure 5: Amplitude of the dynamical thermal conductivity vs $f$, for $f_{np} = 2\%$, $T = 3$K and $R = 5, 7, 10$ nm.

Figure 6: Amplitude of the dynamical thermal conductivity vs $f$, for $f_{np} = 0\%, 2\%$, $T = 300$K and $R = 1, 3$ nm.

Figure 7: Amplitude of the dynamical thermal conductivity vs $f$, for $f_{np} = 0\%, 2\%$, $T = 300$K and $R = 5, 7, 10$ nm.

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Figure 7: Amplitude of the dynamical thermal conductivity vs $f$, for $f_{np} = 2\%$, $T = 300K$ and $R = 5, 7, 10$ nm.

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