Thermal conductivity of Si/Ge superlattices: A realistic model with a diatomic unit cell

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This paper considers the effects of a realistic description of phonons in diamondlike semiconductors and their conversion on the abrupt heterointerfaces on the thermal conductivity of the superlattice (SL). Due to the much larger mass of Ge atoms in comparison to Si, the most probable acoustic phonons in Si layers at room temperature have no counterpart in Ge. In simplified models where Si and Ge are simulated by monatomic crystals with fitted parameters, this leads to the highly efficient trapping of high-energy acoustic phonons in Si layers and drastic reduction of the SL thermal conductivity. The proposed approach incorporates the optical branches and the effective conversion of the phonons at interfaces extends the temperature range for which the model is valid and thereby leads to corrections to predicted thermal conductivity.

Thermoelectric devices based on semiconductor heterostructures attract the attention of industry and science due to potentially superior characteristics.[1] In the design of a prospective thermoelectric device, one needs to focus on the electric part of the problem, where high-quality defect-free superlattices (SL's) can be an advantage, and to engineer a structure with relatively low phonon thermal conductivity that will be able to maintain the temperature gradient produced by the electron flux.

The calculations of the thermal conductivity, performed recently for the simple-cubic model, are reported in Ref. 2. Individual atoms are connected by springs with force constants that reproduce approximately the dispersion of the longitudinal acoustic phonons in constituent materials. Since this very simple model could not provide details of the phonon dispersion spectra, questions are raised about ability of the model to predict thermal conductivity quantitatively. An approach based on the face-centered cubic model of lattice dynamics[3] provides a reasonably accurate description of long-wavelength longitudinal and transverse acoustic phonons in bulk Si and Ge by tuning model parameters. Nonetheless, since the primitive cell of the proposed artificial lattice contains only one atom, optical phonons are altogether absent in such models. At room temperatures ($k_B T \sim 25$ meV) and higher, the optical phonon modes in Si are still not excited, but in Ge, with atoms of much larger mass, the excitation is indeed possible.

At the same time, highly accurate models that mimic both acoustic and optical phonon branches have been proposed (but occasionally not used, to our knowledge, for the calculations of the thermal conductivity in SL's). The dispersion relations for phonons in strained Si and Ge have recently been calculated using an *ab initio* approach.[4,5] The modified Keating model is definitely less fundamental, but it is much simpler to implement, and it was used to examine phonon dispersion in biaxially strained Si and Ge, as well as Si/Ge SL's.[6,7]

The method of valence-force potentials has been successfully applied for the calculation of phonons in bulk diamond,[8] for the analysis of the lattice dynamics and spectroscopic properties of diamondlike crystals,[9] and later, to model phonon dispersions in the Si-Ge strained-layer SL's.[10]

However, it was pointed out[11] that optical modes do not contribute substantially to thermal conduction, since long-wavelength optical phonons have small group velocity. This statement can be essentially relaxed in ultrashort SL's with a period of only a few monolayers. A large number of abrupt heterointerfaces separating narrow layers of semiconductors can lead to the effective conversion of the optical phonons to acoustic ones and vice versa, thus making allowances for the reasonable contribution of these mixed modes to the heat transfer in the SL. Optical phonons close to the edge of the Brillouin zone with noticeable group velocities are excited thermally as well at elevated temperatures and should be accounted for.

We adopt the superior approach based on valence-force potentials for our calculation of the thermal conductivity of diamondlike SL's for thermoelectric applications. Since the method is described quite well in the literature, we recall only the absolutely essential basics of the approach and discuss the complicated and unresolved issues.

A version of the valence-force potential method with six parameters[8] takes into account the change of the lattice potential energy with the change of the interatomic distances (bond lengths) and the angles between adjacent bonds plus cross terms between them. The shortcoming of this model is connected with its neglect of the long-range electrostatic forces and concentrating on only the short-range interactions. Coulomb forces are important when simulating materials like GaAs or BeO; however, they should have a relatively small effect on the phonon dispersion in Si and Ge crystals.

The incorporation of the strain—that is essential for the physics of the Si/Ge heterostructures—into the procedure, originally proposed for bulk semiconductors, is discussed in some detail in Ref. 9. The general conclusion is that there is no straightforward way to modify valence-force parameters to consistently include strain that is inherent in the Si/Ge SL's. For the (001) growth direction the particular parametri-

zation of the constants with the bond length $F=F_0(r/r_0)^n$, where r_0 (r) is the unstrained (strained) bulk interatomic distance, did not give a consistent value for the fitting parameter n. For example, two different fitting parameters n are required for (001)-oriented layers to describe satisfactorily shifts of the longitudinal and transverse phonons with strain in the Brillouin zone center. We make here allowance for the change of interatomic distances due to strain, but not for the modification of the force constants with strain. As more reliable data become available, the calculational procedure can be easily modified to take into account this effect as well.

The primitive cell of the diamondlike crystal permitting comfortable modeling of the heterostructures with (001) interfaces contains two atoms and is defined by the following vectors of the elementary translations:

$$a_1=(0,a_{sub},a_G)/2,$$

$$a_2=(a_{sub},-a_{sub},0)/2, \qquad (1)$$

$$a_3=(a_{sub},a_{sub},0)/2,$$

two of them, a_2 and a_3, lie in the (001) plane. Here $a_G=K(a_{sub}-a_0)+a_0$ is the lattice constant in the growth direction and differs for Si and Ge materials, a_{sub} is the common lattice constant defined by the heterostructure substrate, $K=-2C_{12}/C_{11}$, and C_{ij} are the bulk elastic moduli in standard notation. For a Si/Ge superlattice with $2n/2m$ monolayers, the supercell will have the following translation vector $a_1^{SL}=na_G^{Si}+ma_G^{Ge}$, and the two other (in-plane) vectors a_2 and a_3 will not change.

The phonon thermal conductivity at finite temperature T is given by the formula[3]

$$\kappa=\sum_\lambda \kappa_\lambda, \qquad (2)$$

$$\frac{\kappa_\lambda}{\tau_\lambda}=C_{ph}(\omega_\lambda)v_{\lambda,z}^2, \qquad (3)$$

$$C_{ph}(\omega)=\frac{(\hbar\omega)^2}{k_BT^2}\frac{\exp(\hbar\omega/k_BT)}{[\exp(\hbar\omega/k_BT)-1]^2}. \qquad (4)$$

Here λ specifies the phonon mode in the heterostructure (both polarization and wave vector), $\hbar\omega$ is a phonon energy, τ_λ is a mode lifetime, and $v_{\lambda,z}=\partial\omega_\lambda/\partial q_z$ is a component of the phonon group velocity in the direction of the SL principal axis (001).

Application of this formula requires knowledge of the (mode-dependent) phonon lifetime.[11] This finite lifetime appears primarily due to the anharmonicity of the lattice forces. Note that our quantum-mechanical approach is applicable mostly for ultrashort SL's, where the SL period is smaller than the phonon mean free path (at temperatures in consideration). The crossover between particlelike phonon transport for thick layers and wavelike transport for thin layers is recently documented theoretically.[12] To keep our calculation compact we do not try to consider mechanisms of the phonon decay in SL's and merely assume the same value τ_{ph} of the phonon lifetime for all modes. At the same time, the temperature dependence of the decay processes[13] influences
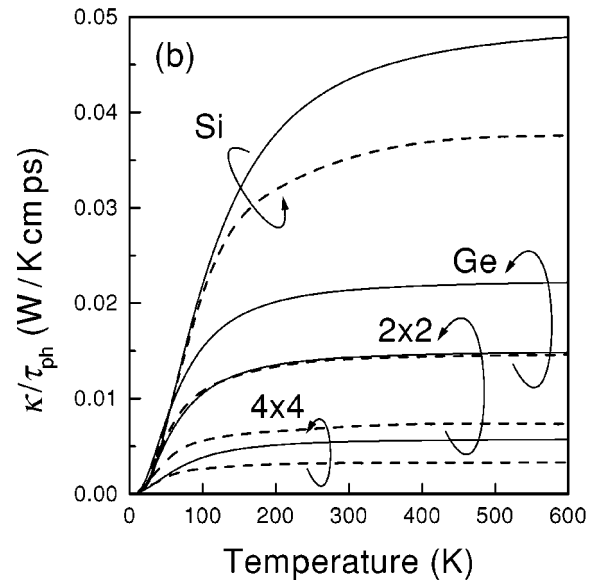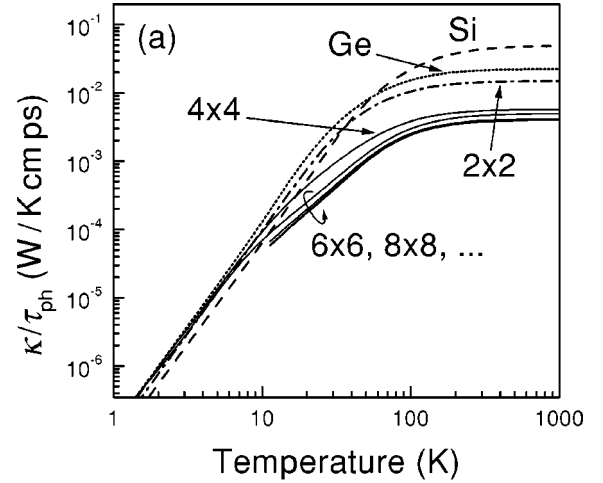

FIG. 1. (a) Thermal conductivity κ normalized to the phonon relaxation time τ_{ph} calculated for bulk Si and Ge, and Si/Ge SL's with 2,4,6,... atomic planes in each heterolayer. (b) Part of the data is shown on the linear plot (solid lines) along with the results of the Ref. 3 (dashed lines).

the thermal conductivity. Herein, we present results for the ratio κ/τ_{ph} as a function of the temperature for different SL's to omit this cumbersome question. As is evident from Eqs. (2)–(4), the calculation of the thermal conductivity requires numerical integration over the Brillouin zone. Some approaches, making this integration more economical for multiatomic complex crystals (and SL's), especially at low temperatures, can be found in the recent Ref. 14.

Figure 1(a) shows results of the calculation of the thermal conductivity for bulk Si and Ge and ultrashort Si/Ge SL's obtained in our realistic diamondlike lattice model. Values of the valence-force constants, lattice parameters, and elastic moduli are taken from Refs. 9 and 10. For both bulk materials and SL's a substrate with the average of Si and Ge lattice constants is assumed. It is found that the modification of the integral with strain is small and hardly deserves more extended discussion here.

The thermal conductivity of Si exceeds that obtained for

the Ge as a result of the much larger atomic weight of Ge ions. But the value of κ/τ_{ph} is even lower for a 2×2 monolayer Si/Ge SL. As the period of the SL becomes larger the thermal conductivity drops more, but quickly (8×8, 10×10 SL's) saturates at values an order of magnitude smaller than bulk Si (room temperature values). This behavior is qualitatively in line with the observation of other authors.[2,3] Here, we shall not compare our results with the oversimplified model of Ref. 2 but instead concentrate on the analysis of similarities and discrepancies with the calculation of Tamura et al.[3]

Figure 1(b) presents part of the information in Fig. 1(a) as a linear plot. Here we compare our data (solid curves) with the results of Ref. 3 (dashed lines). We have reproduced their curves from a graph published in the article,[3] so some minor uncertainties ($\sim5\%$) may result from this procedure. The major difference in the calculated thermal conductivities comes into play mostly at elevated temperatures $T\gtrsim100$K. Our ratio κ/τ_{ph} saturates more slowly in the region of high temperature and consistently reaches somewhat *higher* values. Since the low-energy vibration spectra of the model of Tamura et al. (values of sound velocities) are fitted to the bulk Si and Ge, we believe that this difference comes from the more accurate dispersion of phonon branches at larger wave vectors and, to some extent, thermal conductivity through the (mostly close to the Brillouin zone edge with lower energies and noticeable group velocities) optical phonon modes. As these modes become excited at elevated temperatures, they contribute to the thermal conductivity of bulk materials and heterostructures.

As one compares the position of the 2×2 SL line with the corresponding curve of the Ref. 3 (in the original labeled 1×1 due to the specifics of their simplified model with only one atom in the unit cell), it is evident that our calculation gives a much higher thermal conductivity (and much closer to κ/τ_{ph} for Ge as well), presumably due to the possibility of mixing of acoustic modes in the Si layer to the optical branches in Ge with the corresponding energies at the abrupt interfaces in the heterostructure. We would also like to mention that both atomic planes in each layer belong to the interfaces and experience modified surrounding, so data for the 2×2 SL can be more sensitive to the procedure of parameter averaging at interfaces than for longer-period SL's.

The published experimental results (Ref. 15, for example) are rather scattered and usually address Si/Ge SL's with longer periods >30–50 Å. Though obtaining qualitative agreement (the thermal conductivity in Si is larger than that in Ge and for SL's κ is essentially reduced if compared to bulk materials), we do not risk performing a quantitative comparison here. One of the problems is the above-mentioned simplification concerning the phonon lifetime. Mini-umklapp scattering processes and scattering on the in-
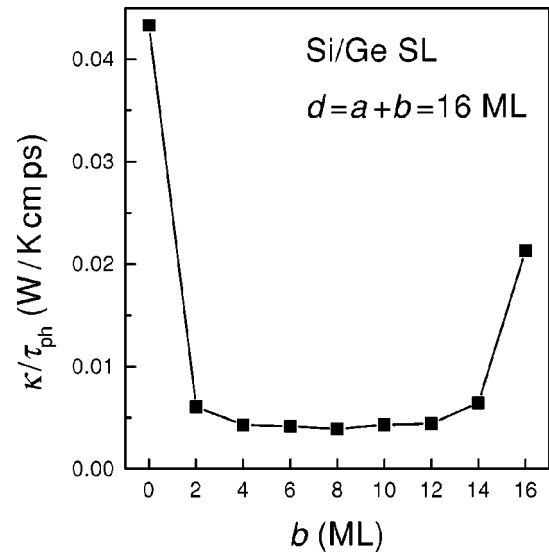

FIG. 2. The ratio κ/τ_{ph} for the Si/Ge (001) SL's with a period d of 16 atomic planes and different widths of Si and Ge layers at $T=300$ K as a function of the Ge thickness b. Pure Si corresponds to $b=0$ and pure Ge is obtained for $b=16$ monolayers.

terface imperfections can influence τ_{ph} and even make it mode-dependent. Second, part of the data points is obtained for the SL's with layer widths exceeding critical thicknesses, so the phonon thermal conductivity can be affected or even defined by a high density of extended defects. In addition, a crossover to the particlelike phonon transport should take place for thicker layers.[12]

To check what heterostructure parameters are the most important for the phonon thermal conductivity we decided to calculate κ/τ_{ph} for the SL with 16 monolayers in the period and different thicknesses a and b of constituent Si and Ge layers. The result of our calculation at $T=300$ K is presented in Fig. 2. The Ge layer thickness $b=0$ corresponds to the bulk Si (strained to fit the average in-plane lattice constant). Strained bulk Ge is obtained for $b=16$. As one can see, only a very weak dependence on the layer thicknesses is obtained as long as $a,b\geq4$. Even for a or $b=2$, when both atomic planes belong to the interface monolayers, with modified surrounding the thermal conductivity is already close to the SL values. Thus, we conclude that the critical property of the SL is the dissimilarity of the phonon spectra of the constituent materials, not the layer thicknesses. This opens the possibility of incorporating ultranarrow subcritical layers of very dissimilar materials, like C into Si/Ge heterostructures, in order to further suppress phonon transmission through the heterostructure.

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