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Enhancement of the thermoelectric figure of merit of $Si_{1-x}Ge_x$ quantum wires due to spatial confinement of acoustic phonons

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Abstract

We have theoretically investigated the thermoelectric figure of merit of $Si_{1-x}Ge_x$ quantum wires rigorously taking into account spatial confinement of both electrons and phonons. The calculations were carried out for cylindrical quantum wires with radius 1.5 nm $< a <$ 15 nm and infinite potential barriers. A significant enhancement of the thermoelectric figure of merit is predicted despite the decrease of the carrier mobility in very narrow-quantum wires. The enhancement is mostly due to the drop in the lattice thermal conductivity caused by the spatial confinement of acoustic phonons and the corresponding increase in phonon relaxation rates. The predicted increase is important for the anticipated applications of $Si_{1-x}Ge_x$ nanostructured materials for high-temperature thermoelectric devices.

Keywords: Thermal conductivity; Phonons; Thermoelectrics; Quantum wires; Spatial confinement

1. Introduction

Continuous progress in growth and self-assembly techniques for synthesizing quantum wires (quasi one-dimensional structures) [1] has stimulated a large body of work pertinent to these systems. Regular electron-beam lithography and wet etching allow now to fabricate quantum wires with widths down to 100 A [2]. Clever techniques employing MBE growth of a narrow gap semiconductor on V-groove surfaces of a wider gap semiconductor have yielded quantum wires of unprecedented quality [3]. Carbon nanotubes are another example of quantum wires. The availability of such systems has resulted in a commensurately increased interest in their optoelectronic and thermoelectric properties.

Recently, there have been increasing number of studies on the modification of thermal conductivity [4] and the enhancement of the thermoelectric figure of merit $ZT = S^2\sigma T/k$ in quantum wires (S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and $k = k_e + k_l$ is

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the sum of electron and lattice contributions to the thermal conductivity) [5,6]. A large value of ZT (up to 14 at room temperature) was predicted for a Bi_2Te_3 quantum wire with width $a = 5$ Å [5]. The figure of merit of a quantum wire superlattice ($a = 20$ Å) was also shown to increase about 2.5 times from its bulk value of $ZT_{3D} = 0.53$ [6]. In all cases the predicted increase came as a result of carrier confinement and corresponding enhancement of the electron density of states near the Fermi level. The carrier mobility and lattice thermal conductivity were assumed to be equal to their corresponding bulk values [5,6].

More recently, Casian et al. [7] argued that decrease of the carrier mobility, which is expected in quantum wires of finite dimensions, may significantly offset the predicted increase of ZT in quasi one-dimensional structures. A strong drop in the electron (hole) mobility at room temperature in quantum wires of finite dimensions is explained by increased electron (hole) scattering on acoustic and optical phonons due to electron (hole) spatial confinement. Using the relaxation-time approximation, Sanders et al. [8] predicted decrease of the electron mobility in a Si quantum wire from 120 cm^2/Vs to < 15 cm^2/Vs when the wire width decreases from 23 to 10 A. This trend can only be reversed at low enough temperature when the elastic (impurity) scattering is a dominant scattering mechanism, and restriction of the phase space due to the spatial confinement leads to the mobility increase. The latter is a well-known Sakaki's result [9], which does not apply to the conditions of high-temperature thermoelectric applications of SiGe structures.

The studies on the thermoelectric figure of merit of quantum wires, reported in Refs. [5–7], had not included modification of the lattice thermal conductivity in quantum wires due to spatial confinement of phonons. This simplification is only valid for quantum wire structures with boundaries made out of material with similar crystalline and elastic properties such that phonon modes extend through the boundaries and do not differ significantly from the bulk. The situation is different for the quantum wires, which are either free-standing or embedded within material with distinctively different elastic properties (like Bi wires in alumina template). Here, phonon dispersion and group velocities are changed due to the spatial confinement induced by the boundaries. The phonon confinement affects all phonon relaxation rates, and makes the thermal transport properties of quantum wires rather different from those of bulk material in much the same way as in quantum wells (thin films) [10,11].

In this paper we theoretically investigate the thermoelectric figure of merit of $Si_{1-x}Ge_x$ quantum wires rigorously taking into account spatial confinement of both electrons and phonons. Particular emphasis is given to the study of interplay among three factors: (i) increased electron density of states, (ii) decreased mobility, and (iii) decreased lattice thermal conductivity. The first two factors are due to spatial confinement of electrons, the last one is due to spatial confinement of phonons. The rest of the paper is organized as follows. In Section 2 we present our theoretical model for the thermoelectric figure of merit. The results of numerical simulation and discussion are presented in Section 3. We give our conclusions in Section 4.

2. Model

As an example system, we consider a $Si_{1-x}Ge_x$ quantum wire structure. The material system is chosen because of its bulk superior high-temperature thermoelectric properties. The mole fraction x of Ge is added to additionally decrease the lattice thermal conductivity, and to facilitate the integration of the quantum wires into a SiGe quantum wire superlattice. At the same time, the presented model will be applicable for other materials. Our model will use the derivations of the thermoelectric parameters for one-dimensional (1D) structures given in Ref. [5]. However, we do not assume that the lattice thermal conductivity k_l equals to its bulk value. Rather, we calculate k_l as a function of the wire radius a and temperature T.

Let us consider a quantum wire of circular cross-section that has a radius a and an infinite length along the x-axis. We assume that the wire has infinite potential barriers and only one occupied electron subband. The latter assumption is rather realistic for narrow wires with 1.5 nm $< a <$ 15 nm. The energy spectrum for this wire can be written as [12]

$$E_{sn}(k_x) = E(k_x) + \frac{h^2}{2m^*}(X_n^s/a)^2, \tag{1}$$

where s is the azimuth quantum number ($s = 0, \pm1, \pm2, \ldots$), n is the radial quantum number ($n = 1,$

$2,3\ldots$), k_x is the axial electron wave vector, X_n^s is the nth zero of the Bessel function of the first kind, $E(k_x)$ is the electron kinetic energy along with the x direction, and m^* is the electron effective mass.

The general expressions of S, σ, k_e for bulk (3D), quantum well (2D), and quantum wire (1D) were derived using relaxation-time approximation [5,13]. In order to investigate the influence of the spatial confinement in a quantum wire on the ZT value, it is convenient to use the ratio between the wire and bulk parameters denoted by indices 1D and 3D, respectively

$$\frac{S^{1D}}{S^{3D}} = \left(\frac{3F_{1/2}(\eta^{1D})}{F_{-1/2}(\eta^{1D})} - \eta^{1D}\right)\left(\frac{5F_{3/2}(\eta^{3D})}{3F_{1/2}(\eta^{3D})} - \eta^{3D}\right)^{-1},$$

$$\frac{\sigma^{1D}}{\sigma^{3D}} = \frac{\pi h^2}{a^2 k_B T (m_y m_z)^{1/2}} \frac{\mu_x^{1D}}{\mu_x^{3D}} \frac{F_{-1/2}(\eta^{1D})}{F_{1/2}(\eta^{3D})},$$

$$\frac{k_e^{1D}}{k_e^{3D}} = \frac{6\pi h^2}{a^2 k_B T (m_y m_z)^{1/2}} \frac{\mu_x^{1D}}{\mu_x^{3D}} \times \left(\frac{5}{2}F_{3/2}(\eta^{1D}) - \frac{9F_{1/2}^2(\eta^{1D})}{2F_{-1/2}(\eta^{1D})}\right) \times \left(\frac{7}{2}F_{5/2}(\eta^{3D}) - \frac{25F_{3/2}^2(\eta^{3D})}{6F_{1/2}(\eta^{3D})}\right)^{-1}, \quad (2)$$

where the Fermi–Dirac function F_i is given by

$$F_i = F_i(\eta) = \int_0^\infty \frac{x^i \, dx}{e^{(x-\eta)} + 1},$$

with $\eta = \zeta/\kappa_B T$ being the reduced chemical potential (relative to the edge of the conduction band), T is the temperature, k_B is the Boltzmann constant, h is the Plank constant, $m_x,\ m_y,\ m_z$ are the components of the effective-mass tensor, and μ_x is the mobility in the x direction. The reduced chemical potentials of the bulk and quantum wire are related as

$$\eta^{1D} = \eta^{3D} - \frac{h^2}{2m^* k_B T}(X_n^s/a)^2. \quad (3)$$

For the fixed values of T and a, the reduced chemical potential depends on the doping level. The latter is used in order to maximize the ZT value. The maximum ZT values, which correspond to the optimized reduced chemical potential, will be denoted by the index "opt".

As we mentioned in the introduction, the reduction of the carrier mobility in a quantum wire of finite dimensions is caused by the spatial confinement of carriers. At room temperature, the dominant electron scattering processes are the longitudinal optical and acoustic phonon scattering processes [7,8]. In this work, we use formulas derived in Ref. [7] under the assumption that spatial confinement of electrons does not significantly alter the electron–phonon scattering rates as it was shown in Ref. [14]. At the same time, spatial confinement of phonons does change their Umklapp and point defects scattering rates [10,11], which will be included in the model when calculating the lattice thermal conductivity. It turns out that in a wide range of the quantum wire radii (from 10 to 150 A), the acoustic phonon limited mobility is approximately equal to the optical phonon limited mobility and is given as [7]

$$\frac{\mu_{1D}}{\mu_{3D}} = 8K_1(h\omega_0/(2k_B T)) \left[3\int_0^\infty dx\, E_1\left(\frac{a^2 x}{2l^2}\right) \times \exp\left(\frac{a^2 x}{2l^2} - \frac{h\omega_0}{2k_B T x} - \frac{h\omega_0 x}{8k_B T}\right)\right]^{-1}, \quad (4)$$

where K_1 is the modified Bessel function of the second kind [15], E_1 is the exponential integral function [15], parameter $l = h/m_x\omega_0$, and ω_0 is the limiting phonon frequency related to the Debye temperature.

Another important factor, which we include in our model, is the modification of the lattice thermal conductivity due to the spatial confinement of acoustic phonons. The bulk of heat in silicon and germanium structures is carried by acoustic phonons within a small region in the first Brillouin zone. It was shown by Balandin and Wang [10] that phonon modes within this region are subject to a significant modification in a quantum-well structure, which leads to a strong drop in the lattice thermal conductivity. We expect that in a quantum wire the effect will be even stronger [16].

It is well known that the lattice (phonon) thermal conductivity is written as $k_{ph} = \frac{1}{3}\Sigma S(\omega) v_g \Lambda(\omega)\, d\omega$, where $S(\omega)$ is the contribution to the specific heat per frequency interval from phonons of frequency $w, \Lambda(\omega)$ is the phonon mean free path (attenuation length), and v_g is the phonon group velocity. Using the relaxation-time methods [17,18], the expression for k_{ph} we can be further rewritten as [17]

$$k_l = \frac{k_B}{2\pi^2 v_g}\left(\frac{k_B}{h}\right)^3 T^3 \int_0^{\theta/T} \frac{\tau_C x^4 e^x}{(e^x - 1)^2}\, dx, \quad (5)$$

where $x = h\omega/k_B T$, θ is the Debye temperature, τ_C is the combined relaxation time due to different scattering mechanisms, and v_g is the phonon group velocity which is a function of the wire radius and boundary conditions at the wire interface [10,16]. Eq. (5) was written under assumption that the resistive scattering processes are dominant [17]. The combine relaxation time is defined as

$$\frac{1}{\tau_C} = \frac{1}{\tau_U} + \frac{1}{\tau_B} + \frac{1}{\tau_M}, \tag{6}$$

where $1/\tau_U$, $1/\tau_B$ and $1/\tau_M$ are the phonon relaxation rates which correspond to the three-phonon Umklapp scattering, boundary scattering, and scattering on point defects (mass-difference or impurities, isotopes, etc.), respectively. These scattering processes are known to be dominant for crystalline Si, Ge, and Si_xGe_{1-x} low-dimensional structures at room temperature and above. Each of these relaxation times is a function of the phonon group velocity [17]. For example, phonon scattering rate on point defects (mostly isotopes) is inversely proportional to v_g^3. For this reason, even small variation of the phonon group velocity will lead to a significant change in the lattice thermal conductivity [10,11,16].

The boundary scattering in our model is treated in the Casimir limit. It implies that all phonons that have a positive normal velocity lose the sense of their directionality and obey the equilibrium distribution when they reach the boundary. It can be shown that the effective boundary mean free path for a cylindrical quantum wire of diameter D in the Casimir limit is given by $L_O = D$ [18]. Thus, we write the phonon-boundary scattering rate for a cylindrical quantum wire as $1/\tau_B = v_g/D$. More accurate treatment of phonon-boundary scattering that includes partially diffuse and partially specular interfaces has been carried out by Chen [19,20].

In order to obtain the phonon group velocity $v_g = \partial\omega/\partial q$ (where q is the phonon wave vector), one has to calculate exact dispersion relations for the phonon propagation modes in a cylindrical wire. Details of such calculations are reported by us elsewhere [16]. Here, we illustrate the procedure using the example of the clamped surface boundary condition. These boundary conditions correspond to the experimental situation when a quantum wire is embedded within more rigid material. Qualitatively it can be characterized by a significant difference in acoustic impedance for the wire and cladding materials. In this case, the elasticity equation for the phonon longitudinal waves propagating along the x-axis takes the form [18]

$$q_l^2 \frac{(q_t a) J_0(q_t a)}{J_1(q_t a)} + q^2 \frac{(q_l a) J_0(q_l a)}{J_1(q_l a)} = 0, \tag{7}$$

where q_l, q_t are the parameters which define the phonon dispersion in the quantum wire, q is the x-component of the phonon wave vector. These quantities are related as

$$q_{l,t}^2 = \frac{\omega^2}{v_{l,t}^2} - q^2, \tag{8}$$

where $v_l(v_t)$ is the longitudinal (transverse) sound velocity in the given material. Numerically solving Eqs. (7) and (8) we found the phonon dispersion and average group velocities in the Si_xGe_{1-x} quantum wire as a function of the wire radius a. The obtained data was used to calculate the lattice thermal conductivity [16], and, finally, the thermoelectric figure of merit of a quantum wire.

3. Results of calculations

As it was already mentioned, Si_xGe_{1-x} material system was selected for numerical simulation for its great promise for high temperature thermoelectric applications [21]. We have also already shown [16] that the lattice thermal conductivity of Si_xGe_{1-x} a quantum wire with clamped or free-surface boundaries experiences a huge drop, which makes its value equal to about 1% of the pure silicon bulk value. This drop is caused by the decrease of the phonon group velocity and corresponding increase in the phonon relaxation rates. The mass-difference scattering due to the presence of Ge atoms ($m_{Ge} = 3m_{Si}$) additionally contributes to the thermal conductivity decrease. We have chosen 10% Ge content since it deteriorates the lattice thermal conductivity and at the same time does not dramatically reduce the electron mobility, which is about 50% of its pure Si value at this concentration.

For numerical simulation, we assume that the x direction coincides with [1 0 0], so that $m_x = (2m_t + m_l)/3$, where $m_l = 0.9163m_0$ and $m_t = 0.1907m_0$ are the bulk longitudinal and transversal effective masses, respectively. For the first zero of $J_0(X)$ we

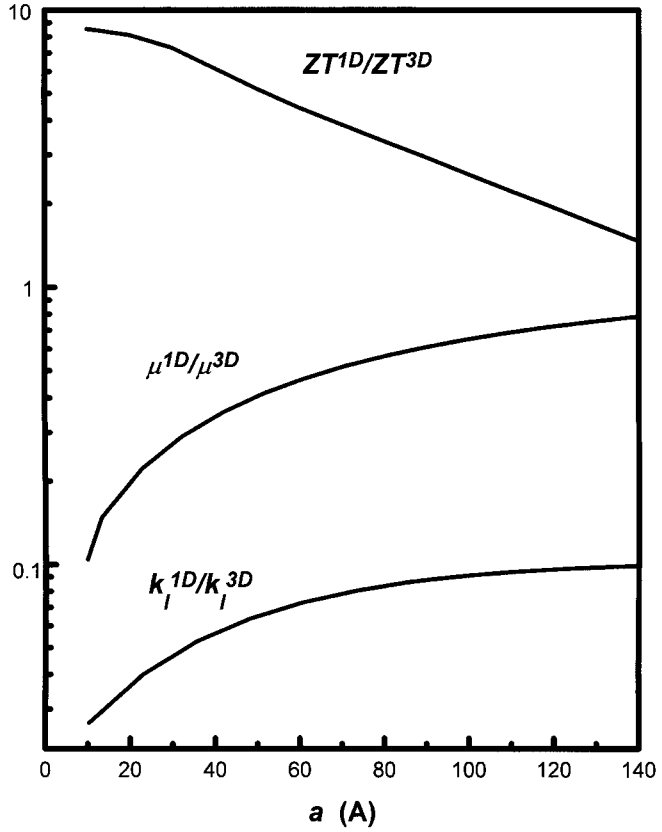

Fig. 1. Calculated mobility, lattice thermal conductivity, and thermoelectric figure of merit of the $Si_{0.9}Ge_{0.1}$ quantum wire as the functions of its radius a. Results are shown for room temperature. Note that the increase of ZT is mostly due to the spatial confinement of the acoustic phonon modes and corresponding decrease in the lattice thermal conductivity.

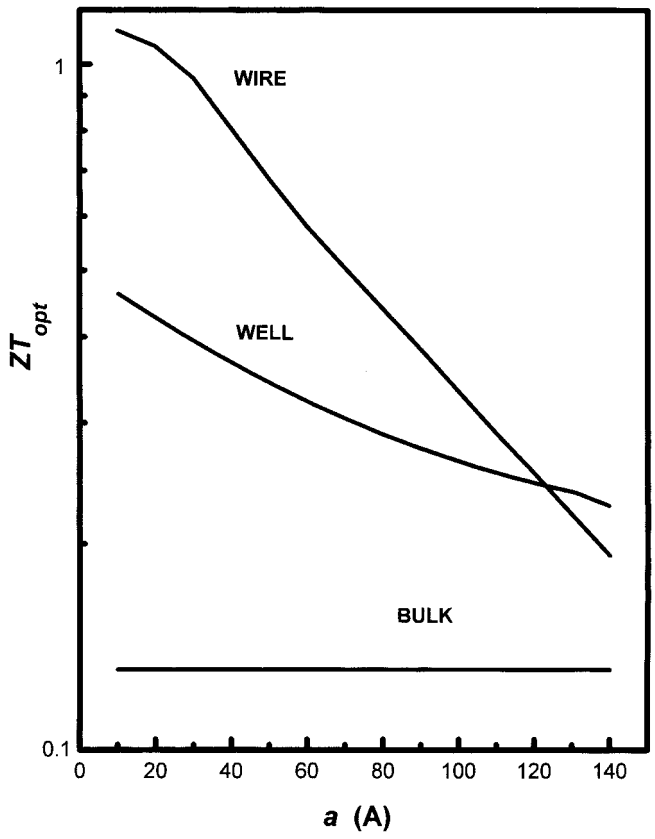

Fig. 2. Calculated thermoelectric figures of merit of the $Si_{0.9}Ge_{0.1}$ quantum well and quantum wire as the functions of thickness and radius a, correspondingly. Results are shown for room temperature.

take $s = 0$, and $n = 1$ in Eq. (1), and $X_1^0 = \sqrt{6}$. We also assume that $\theta = 625$ K, and $v_l = 8.47 \times 10^5$ cm/s, $v_t = 5.34 \times 10^5$ cm/s.

In Fig. 1 we depicted the carrier mobility and lattice thermal conductivity normalized to their bulk values as functions of the wire radius. One can see a significant decrease of both of these quantities, especially at the wire radii $a < 40$ A. One should mention here, that the behavior of the mobility μ and the lattice thermal conductivity k_l are not directly related. The decrease in μ comes about as a result of the increased electron–phonon scattering rates due to electron confinement, while the decrease of k_l is a result of the increased phonon relaxation due to phonon spatial confinement [10,11,16]. In principle, one can design a low-dimensional structure with strong phonon confinement but without electron confinement and vice versa. The structures where both electrons and phonons should be considered as spatially confined constitute one of the most interesting material systems currently being studied for thermoelectric applications [21–24].

As it is shown in Fig. 1, ZT increases with decreasing wire radius but starts to saturate at the wire radius $a = 20$ A. This saturation is caused by the sharp mobility decrease. The calculation of ZT^{1D} value was carried out for the same doping level as for ZT_{opt}^{3D} and, thus, the curve presented in Fig. 1 does not correspond to $ZT_{opt}^{1D}/ZT_{opt}^{3D}$. In order to find the optimum ZT_{opt}^{1D} value, the doping concentration for the quasi-1D case should be additionally optimized. It is interesting to note that despite the similar behavior of the ZT curve with the one presented in Ref. [5], the increase in ZT in our case is mostly due to the decrease of the lattice thermal conductivity rather than increased electron density of states [5,6]. The overall improvement of ZT came despite predicted decrease of the carrier mobility [7], which was included in our model.

In Fig. 2 we show the maximum expected ZT_{opt} values. For this figure, the calculations were performed for the doping levels optimized for each particular wire radius a. The data for the $Si_{0.9}Ge_{0.1}$ quantum well was obtained on the basis of the model reported by Balandin and Wang [11]. One can see that decrease of the dimensionality brings enhancement of the thermoelectric figure of merit despite predicted decrease of the carrier mobility [7,8] mostly because of the spatial confinement of acoustic phonons and corresponding drop in the lattice thermal conductivity. This is an important result, since it may shift the emphasis from the quantum confinement of carriers to engineering of phonon modes in order to achieve high ZT. At the wire radius of about 120 A, the ZT values for a quantum wire and a quantum well become approximately equal. So that in order to take advantage of stronger spatial confinement effects in quantum wires, their radius should be in the range of 10 nm or smaller.

4. Conclusion

We have studied the thermoelectric figure of merit of $Si_{1-x}Ge_x$ quantum wires rigorously taking into account spatial confinement of both electrons and phonons. A significant enhancement of the thermoelectric figure of merit (order of magnitude) is predicted despite the decrease of the carrier mobility in very narrow quantum wires. The enhancement is mostly a result of the drop in the lattice thermal conductivity caused by the spatial confinement of acoustic phonons and the corresponding increase in phonon relaxation rates. The predicted increase is important for the anticipated applications of $Si_{1-x}Ge_x$ nanostructured materials for high-temperature thermoelectric devices.

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