مجلة ابن الهيثم للعلوم الصرفة والتطبيقية   المجلد23 (1) 2010

تأثير احتجاز الفونون في التوصيلية الحرارية لشبيكة

Zn_4Sb_3 ذي تركيب بئر كمي

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الخلاصة

تحرينا نظريا التوصيلية الحرارية لشبيكة مستوية ذي تركيب بئر كمي نانومتري منفرد من مادة شبه موصلة Zn_4Sb_3 اخذين في الحسبان تأثير الاحتجاز المكاني للفونونات في بعدين . الحسابات نفذت لتركيب بئر كمي منفرد بسطوحِ حرة بسمك 8.5nm في درجة حرارة الغرفة . وجدنا تخفيضا مهما في التوصيلية الحرارية للشبيكة، وإن هذا التخفيض في الغالب بسبب الهبوط في متوسط سرعةِ المجموعةِ سببها الاحتجاز المكاني للفونونات والزيادة المطابقة في نسبِ إرخاءِ الفونونات . إن النقصانَ المتوقع مهم للتطبيقات المتوقعةِ للنبائط ذي التركيب النانومتري لمادَة Zn_4Sb_3 في درجة حرارة الغرفة . نتائجنا النظرية في اتفاق جيد مع البياناتِ التجريبيةِ المتوافرةِ للتركيب النانومتري لمادَة Zn_4Sb_3 .

Phonon Confinement Effect on Lattice Thermal Conductivity of Zn_4Sb_3 Quantum Well Structure

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Abstract

We have theoretically investigated the in-plane lattice thermal conductivity of Zn_4Sb_3single quantum well structure taking into account spatial confinement of phonons. The calculations were carried out for free-surface quantum wells with thickness 8.5nm in the room temperature. We show that the lattice thermal conductivity is a significant reduce. The reduction is mostly due to the drop in the average group velocity caused by the spatial confinement of acoustic phonons and the corresponding increase in phonon relaxation rates. The predicted decrease is important for the anticipated applications of Zn_4Sb_3 nanostructure materials for room-temperature thermoelectric devices. Our theoretical results are in a good agreement with available experimental data for Zn_4Sb_3 quantum wells.

Introduction

Thermoelectric cooler (TEC) devices show excellent cooling performance for the applications where temperature stabilization is required [1]. Some typical uses include cooling of laser diodes, infrared detectors, heat regulators for computer processors, blood analyzers, and portable picnic coolers as well as many other applications in deep space probes. However, they have suffered from low efficiencies to be viable in many commercial fields, such as domestic air conditioning [2]. If the percentage of Carnot efficiency could be improved from 5% to greater than 70%, it would have a stunning impact on the reduction of space and planetary probe [3].

The usefulness of thermoelectric materials for the applications is typically expressed by the dimensionless quantity ZT, where T is absolute temperature (in Kelvin) and Z is the thermoelectric figure of merit [4]: $Z = S^2 \sigma/\lambda$. Here S is the thermoelectric power or Seebeck coefficient, σ is the electrical conductivity and λ is the total thermal conductivity (λ□= λ_L + □ λ_E; the lattice and electronic contributions respectively)[5, 6, 7]. The development of a material braking the relationship between these transport properties[8].Recently, several promising compounds that contain the semi-metal antimony have been shown to have good thermoelectric characteristics such as Zn_4Sb_3 and $CoSb_3$, with the highest ZT values being 1.350 at 400°C and 0.872 at 600°C [5].

One approach being pursued for increasing ZT is use of low-dimensional structures, as realized in the form of quantum wells structures with free-surface or rigid boundaries to provide a promising strategy for designing materials with a large thermoelectric figure of merit [9,10]. In both free-surface or rigid boundaries, spatial confinement of acoustic phonons changes the phonon dispersion relation, which may make a modification of the average group velocity and affect all phonon relaxation rate [11,12]. Some of researches experimentally investigated the thermal conductivity of Zn_4Sb_3 membranes were measured with a suspended microstructure [5,7]. An extremely large reduction of λ_L (more than an order of magnitude) was observed in the room temperature range. The current project goal was devoted theoretically to investigate the lattice thermal conductivity of this compound in two-dimension quantum well taking into account modification of the acoustic phonon modes and phonon group velocities in free surface wells due to spatial confinement effects. The results of numerical simulations presented below were obtained for a free-standing quantum well since the boundary conditions for the elasticity equation are the simplest in this case.

Theory

Calculation of the lattice thermal conductivity

It is well known that the lattice thermal conductivity arises due to phonon relaxation rates corresponding to the different scattering processes, which do not conserve crystal momentum [13]. Such processes are boundary scattering, τ_B, mass-difference scattering, τ_M, (isotope, impurities, etc.), and phonon anharmonic interactions (three-phonon Umklapp processes, τ_U). If we consider a high-quality material, the impurity scattering mechanisms can be strongly reduced except for the isotope scattering, τ_I. As the scattering processes depend on the phonon wave vector, additional dispersion and phonon group velocity modification arise. To take into account this modification, we use the Callaway's expression for the lattice thermal conductivity under the assumption that the resistive processes are dominant [14]:

$$\lambda_L = \frac{K_B}{2\pi^2 V}\left(\frac{K_B}{\hbar}\right)^3 T^3 \int_0^{\theta/T} \frac{\tau_C x^4 e^x}{(e^x - 1)^2}\,dx \qquad (1)$$

where K_B is Boltzmam's constant, $\hbar$ is Plank constant divided by 2π, τ_C is the combined phonon relaxation time due to all resistive processes, θ is Debye temperature, and $x = \hbar\omega/K_B T$. The mean velocity V is calculated for all phonon polarization types from the expression[15]: $3V^{-3} = V_L^{-3} + 2V_T^{-3}$.In order to determine the resistivity of a single quantum well to crystallineZn_4Sb_3, only three major contributions which the above mentioned has to be considered, we proceed with the Matthiessen's rule [16]: $\tau_C^{-1} = \tau_U^{-1} + \tau_I^{-1} + \tau_B^{-1}$.

The relaxation rate of the Umklapp process can be expressed in the form [17];

$$\tau_U^{-1} = \frac{2\gamma^2 K_B T \omega^2}{\mu V_o \omega_D} \qquad (2)$$

where γ is the Gruneisen parameter, μ is the shear modulus, ($V_o = \frac{3a^2c}{n_c}\sin 60$) is the volume per atom, here a and c are lattice constants and n_c the number for atoms per unit cell ($n_c = 6$ for the hexagonal cell), and ω_D is the Debye frequency.

The important fact is that the Isotope scattering rate which arises due to interaction with atoms of mass-different from the average atomic mass, M, in a semiconductor is very sensitive to the average group velocity of the confined phonon. The phonon relaxation rate in the Isotope scattering is given by. [17];

$$\tau_I^{-1} = \frac{V_o \omega^4}{4\pi v_g^3}\sum_i f_i[1 - (M_i/M)]^2 \qquad (3)$$

where M_i is the mass of an atom, f_i is the fractional content of atoms with mass M_i which is different from M of the main atom.

The most general expression for the phonon-boundary scattering rate can be written in the Casimir limit for free-surface quantum well as [18]:

$$\tau_B^{-1} = \frac{v_g}{W} \qquad (4)$$

where W is the well width.

Confinement of acoustic phonons

The expression for the relaxation rates in Eqs. (2)- (4), contains only a few parameters. The parameter $v_g(q)$ is very important but is governed by the well width W. The dispersion of the confined phonon modes is found from the elastic wave equation in the isotropic continuum approximation [19]:

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = v_t^2 \nabla^2 \mathbf{u} + (v_l^2 - v_t^2)\,\text{grad div}\,\mathbf{u} \qquad (5)$$

where u is the displacement vector, and $v_l(v_t)$ is the speed of longitudinal (transverse) acoustic waves in bulk media. The longitudinal waves are coupled modes of axial and radial modes that have the quantized wave vectors $q_l$andq_t , respectively [18].

To define a system of the confined modes, Eq. (1) should be complemented by the boundary conditions at the film surfaces $z - \pm a/2$ [19]. The dispersion relations of confined phonons are obtained from the solution of Eq. (5) subject to the boundary condition that free-surface is known from acoustics and is not reproduced here. But here we summarize the obtained results for the spectrum of the acoustic phonons in free-standing films.

There are three different types of confined acoustic modes in a quantum well characterized by the kind and the symmetry of displacement components [19, 20]:

1- For the first of them, the horizontal shear (S) modes are similar to the transverse (T) modes in bulk semiconductor and have only a nonzero displacement $u_0^{(\perp)}$ which is perpendicular to the direction of wave propagation and lies in the plane of film; $u_0^{(\perp)}(z)$ is either an odd or even function of z. The dispersion relation for the S modes can be written as $\omega_n - s_t\sqrt{q_x^2 + q_{z,n}^2}$, where subscript n denotes different branches of the same polarization type, and the $q_{z,n}$ is quantized as $q_{z,n} = \pi n/W$.

2- For the modes of the second type, the dilatational (D) modes $u_0^{(z)}$ is an odd function of z, while $u_0^{(l)}$ is an even function of z (with respect to the mid-plane). The dispersion equation is [20,18]:

$$\tan\frac{q_t W}{2} + \frac{4q^2 q_l q_t}{(q^2 - q_t^2)^2}\tan\frac{q_l W}{2} - 0 \qquad (6)$$

where q_l and q_t are the parameters which define the phonon dispersion in the quantum well and q is the x-component of the phonon wave vector. These parameters are represented as

$$q_{l,t}^2 = \frac{\omega^2}{v_{l,t}^2} - q^2 \qquad (7)$$

where ω is an angular phonon frequency. Since these types of confined waves have a component in the direction of propagation, they can be viewed as a modification of the bulk longitudinal (L) mode [18].

2- Finally, the third type of modes the flexural (F) modes $u_0^{(z)}$ is even and $u_0^{(l)}$ is an odd function of z.

$$\tan\frac{q_l W}{2} + \frac{4q^2 q_l q_t}{(q^2 - q_t^2)^2}\tan\frac{q_t W}{2} = 0 \qquad (8)$$

For both D and F phonon modes $\omega_0^{(1)} = 0$. In our calculations we have neglected the F mode by analogy with the bulk processes (see Ref.21).

The system algebraic acoustic-wave equations (Eqs.(6) and (7)) may be solved by the numerical approach, and phonon group velocity is calculated for each branch via numerical differentiation. The phonon group velocity for each mode type in the nth branch is defined as $v_n^{s,sh}(q) = \frac{\partial}{\partial q}\omega_n^{s,sh}(q)$[22].

In order to obtain the resulting group velocity we take the average group velocity as a function of phonon energy as follows[22];

$$\bar{v}_g(\hbar\omega) = \frac{\sum_n v_{g,n}(\hbar\omega)N_n(\omega)}{\sum_n N_n(\omega)} \qquad (9)$$

Where $v_{g,n}$ is the group velocity of the nth mode, $N_n(\omega)$ is the number of oscillators with frequency ω on the nth mode. The Boltzmann equation was used to find the relation between the density of oscillators on nth and (n+1)th modes [23].

$$\frac{N_{n+1}}{N_n} \approx e^{-(\hbar\omega)/k_B T} \qquad (10)$$

Averaging over contributions from all branches weighted by the population factor, we obtain the functional dependence of phonon group velocity on phonon energy. The population averaged phonon group velocity is then used to calculate the lattice thermal conductivity.

Results and Discussion

We carry out numerical simulation for Zn_4Sb_3 quantum well by solving Eqs.(6) and (7), using the numerical Newton's method by MatLab software. The solutions yield the dispersion relations ω_n versus q for the 1….n phonon modes. The material parameters used in simulation were the following: $v_l = 3.59 \times 10^5 cm/s$, and $v_t = 2.08 \times 10^5 cm/s$, the lattice constants $a = 12.231Å$ and $c = 12.420Å$, mass of an atom $M = 1.4868 \times 10^{-25}$kg, Gruneisen parameter $\gamma = 1.57$, Debye temperature $\theta = 237K$, and the isotope factor $\Gamma \times 10^4 = 7.23$ for five Zn isotopes (48.89% of Zn^{64}, 27.81% of Zn^{66}, 4.11% of Zn^{67}, 18.56% of Zn^{68}, 0.62% of Zn^{70} and two Sb isotopes (57.25% of Sb^{121}, 43.75% of Sb^{123}). In Figs. 1 and 2, the typical results are shown for the lowest shear phonon modes ($n = 1, \ldots, 9$) of a Zn_4Sb_3 in an85Å wide free-surface layer. For comparison, the calculated dispersion curves and average sound velocities of bulk Zn_4Sb_3 are plotted in all figures, where the doted line represents the bulk data. As seen from these figures, the dispersion curves in quantum well system and then phonon group velocities differ radically from that of bulk.

The phonon group velocities as functions of the phonon wave vector q along the propagation direction of Zn_4Sb_3 quantum well are shown in Fig.2. From this figure we can easily see the general trend:

i. the phonon group velocities are lower than in bulk, and decrease with increasing mode number.

ii. the higher the mode number is, the smaller the group velocity is over the range of wave vector values.

Due to the spatial confinement bring modifications of the energy and momentum conservation laws therefore, many more branches of each polarization type are presented in the quantum well as compared to the bulk. The dispersion and energy curves for the phonon dilatational mode are shown in Figs.3 and 4 for an 8.5nm wide free-surface quantum well. One can see from these Figs. that the phonon properties differ drastically from the bulk (doted line). Once we have found the average phonon group velocity over all contributing modes as a function of the phonon energy, we can obtain the lattice thermal conductivity using Eqs.(2)-(5).

The overall value of the average phonon group velocity is only about half of the bulk phonon group velocity as shown in Fig.5. This is a significant drop.

The overall phonon scattering rate increases in a quantum well. A significant drop in the average phonon group velocity (see Figs.2 & 5) strongly increases phonon relaxation rates via isotope scattering from Eq. (3). The three-phonon Umklapp scattering is also becoming more effective. Boundary scattering is less sensitive to the phonon group velocity change and just slightly offsets the final result. One important thing to note is that by improving surface quality one can reduce the boundary scattering rates but not the Umklapp scattering rate. The increase of the Umklapp process scattering rate in a quantum well is a direct result of the modification of phonon dispersion due to spatial confinement of the phonon modes. One can see that λ_L for a8.5nm (85Å) wide well is much smaller than that of a bulk.

In order to verify the accuracy of our calculation for λ_L, we compare the results with available experimental data. We found that our numerical results are consistent with experimental data presented in Ref.[7]. It was reported there that the lattice thermal conductivity of the Zn_4Sb_3 films (0.5-3 mm thick) is considerably lower than λ_L of bulk crystals of the same solid solution. At room temperature, λ_L =1.2 W/m.K was measured as compared to the bulk value of 1.7 W/m.K. A maximum decrease of about 30% in lattice thermal conductivity is predicted for a Zn_4Sb_3 quantum well compared to the bulk case. It is reasonable to expect that further decrease of the film thickness will bring about an additional decrease in λ_L. Experimentally observed temperature dependence in Ref.[7] is very close to our calculations.

Conclusions

In conclusion, we have theoretically investigated the in-plane lattice thermal conductivity □λ_L of a semiconductor thin films that take into account modification of the acoustic phonon dispersion in this structure as well as phonon redistribution effects due to boundary scattering. According to the results and discussion above, the strong modification of the phonon group velocities and dispersion due to spatial confinement leads to a significant increase of the phonon relaxation rates and, as a result, a strong drop in the lattice thermal conductivity □λ_L.

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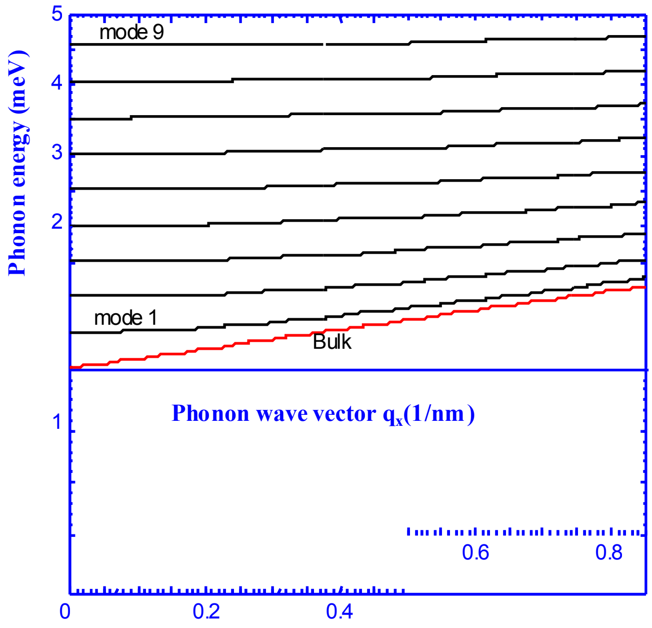

Fig.1: Phonon energies as the functions of the phonon wave vector for the shear mode in a 8.5 nm thick semiconductor slab (quantum well). The results are shown for nine lowest phonon modes. The doted lines show the phonon energy for bulk material.

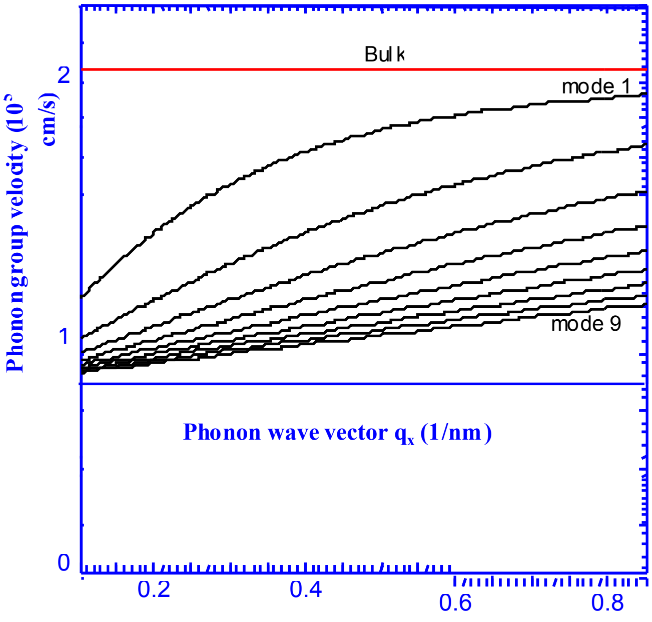

Fig.2: Phonon Group velocities as the functions of the phonon wave vector for the shear mode in a 8.5 nm thick semiconductor slab (quantum well). The doted lines show the average group velocity for bulk material.

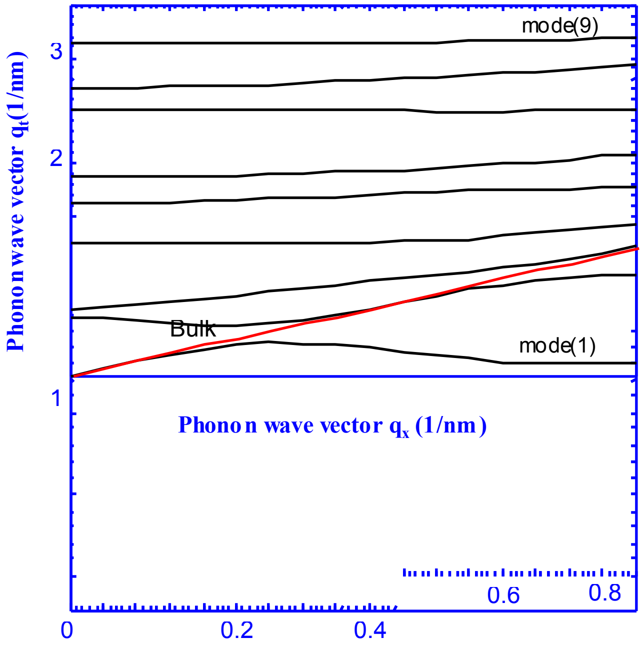

Fig.3: The dispersion function in wave vector space calculated by solving Eq. (6) and (7) numerically for the dilatational mode in a 8.5 nm thick semiconductor slab (quantum well).

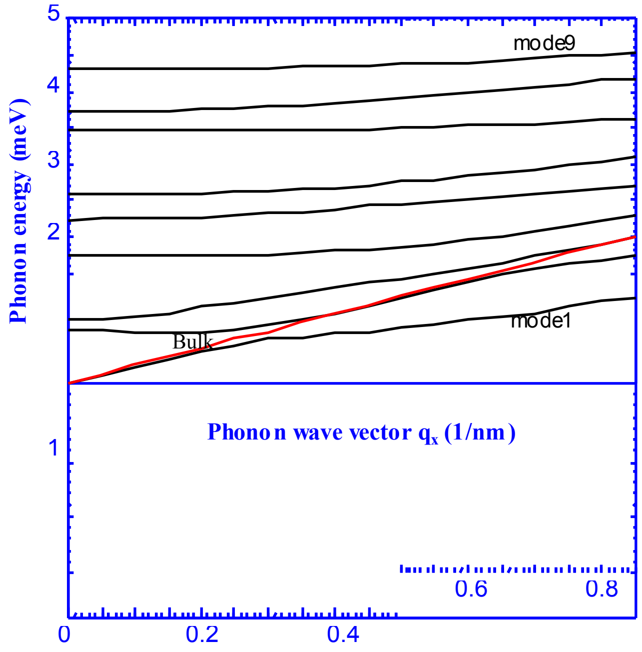

Fig.4: Phonon energies as the functions of the phonon wave vector for the dilatational mode in a 8.5 nm thick semiconductor slab (quantum well).

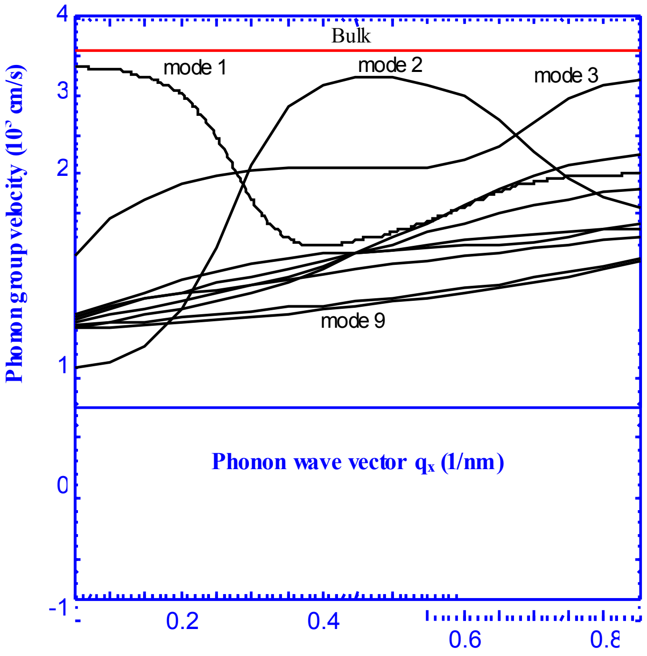

Fig.5: Phonon group velocity as the functions of the phonon wave vector for the dilatational mode. The doted lines show the average group velocity for bulk material.