Thermoelectric Applications of Low-Dimensional Structures with Acoustically Mismatched Boundaries

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It is shown that a finite acoustic mismatch between structure and barrier materials in low-dimensional structures leads to the acoustic phonon confinement, which in its turn brings about a corresponding decrease of the phonon group velocity and modification of the phonon density of states. These factors contribute to the reduction of the in-plane lattice thermal conductivity, thus allowing one to increase the thermoelectric figure of merit. Results of experimental study of confined acoustic phonons in single Si thin films and Si/Ge superlattices are also reported. High-resolution Raman spectroscopy of ultra-thin silicon-on-insulator structures reveals multiple peaks in the spectral range from 50 cm^{-1} to 160 cm^{-1}. The peak positions are consistent with the theoretical predictions and indicate the confined nature of phonon transport in thin films and superlattices with a finite acoustic mismatch between layers. This opens up a novel tuning capability for optimization of the thermoelectric properties of low-dimensional structures.

I. INTRODUCTION

We have recently predicted theoretically that confinement of acoustic phonons in semiconductor structures brings about significant modification to their thermoelectric properties [1-4]. The predicted increase of the thermoelectric figure of merit in quantum wells with free-surface boundaries has been a result of a significant drop of the phonon group velocity due to spatial confinement [3]. The change in phonon dispersion (phonon mode quantization) leads to a decrease in the group velocity, a corresponding increase of the phonon relaxation rates and thus, to a strong drop of the *in-plane* lattice thermal conductivity. This mechanism is different from phonon wave interference that requires length scale comparable to the phonon coherence length [5]. It is, in essence, a decrease of the lattice thermal conductivity due to the change in the acoustic phonon dispersion. The latter can play an important role even at high temperatures provided that there is a significant acoustic impedance mismatch

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between the material of a low-dimensional structure (quantum well or quantum wire) and the surrounding barrier material.

An ability to modify the lattice thermal conductivity opens up an additional degree of freedom for maximizing the thermoelectric figure of merit $ZT=S^2\sigma/(K + K_e)$. Here S is the Seebeck coefficient, σ is the electric conductivity, K is the lattice thermal conductivity, and K_e is the electronic thermal conductivity). This modification of the thermoelectric figure of merit due to the change in K value comes in addition to earlier predicted increase due to increased phonon-boundary scattering in thin-films [6] and in quantum wires [7]. The *perpendicular* thermal transport in Si/Ge superlattices was also shown to be suppressed at high temperature due to the acoustic mismatch at the boundaries [8].

The theoretical models developed in Refs. [2-3] have used a simplifying assumption that the boundaries of low-dimensional structures are either free- or clamped-surface boundaries. The former corresponds to a free-standing thin film (or thin film embedded within "soft" material like polymer), the latter corresponds to the thin film embedded within rigid material. Most of the real experimental situations fall into the category of intermediate (or mixed) boundary conditions. This allows for a partial phonon wave function penetration through the boundaries. Quantitatively the difference in the "rigidity" of materials can be characterized by the acoustic mismatch between acoustical impedances of the corresponding materials $\zeta=\rho_2 V_2/\rho_1 V_1$, where ρ_i is the density of i*th* material and V_i is its sound velocity. Even similar materials may have rather large acoustic mismatch ζ. For example, mismatch between Si and Ge calculated for longitudinal and transverse sound velocities is 0.75 and 0.71, respectively. Here I used parameters of Si and Ge summarized in Table I. The mismatch between two very similar materials such as GaAs and $Al_xGa_{1-x}As$ for a 50% alloy lies in the region of 0.90. Even this relatively small mismatch has led to a frequency selective phonon transmission in a superlattice [5]. It is natural to assume that the acoustic mismatch in many other thermoelectric materials based on low-dimensional structures will be much larger. This should be particular true for materials of dissimilar crystalline properties such as array of single-crystal Bi wires imbedded in alumina template recently suggested for thermoelectric applications [9] or Bi_2Te_3 thin films on polymer substrate [10].

Thus, it is important to determine experimentally if the finite acoustic mismatch leads to quantum confinement of acoustic phonons in low dimensional structures. Previously, modification of acoustic phonon modes has been extensively studied in superlattices. Such modification was evident by appearance of the folded phonon doublets in Raman spectra [11]. In this case, the phonon modes penetrate through several layers of materials (partially confined), and the doublets originate due to additional periodicity of the superlattices. The phonon dispersion in superlattices can be theoretically described by Rytov's model [12]. Spatial confinement of phonons in

Raman spectra of a *single thin film* has not been experimentally investigated yet [13]. This is primary due to the lack of high quality thin films with sharp interfaces embedded within material with distinctively different elastic properties. In most of cases, one deals with quantum wells grown on material with very similar crystalline structure. Here I present the report of the observation of confined acoustic modes in single thin silicon film embedded in silicon dioxide.

The rest of the paper is organized as follows. Chapter II presents a simple model for the lattice thermal conductivity of a quantum well (thin film) that allows one to take into account the effects of acoustic phonon confinement. In section B of this chapter, I give an analytical expression for a phonon group velocity of shear modes that illustrates a decrease of the in-plane phonon velocity due to confinement in perpendicular (growth) direction. Chapter III presents results of Raman spectroscopy study of acoustic phonon confinement in single Si films embedded into silicon dioxide and acoustic phonon folding in Si/Ge superlattices designed for thermoelectric applications. A discussion and comparison with available thermal conductivity data follow the spectroscopy data. Conclusions are given in Section IV.

II. THEORY

A. Calculation of the lattice thermal conductivity

A simplified theory that allows one to include affects of phonon confinement can be presented as follows. The lattice thermal conductivity K at a temperature T is given by the formula

$$K = \frac{1}{(2\pi)^3} \int V_G^2 (\cos\varphi)^2 \tau_C(q) C_{ph}(q) d^3q,$$

(1)

where V_G is the phonon group velocity, ϕ is the angle between the group velocity and the direction of the heat flow, q is the phonon wave vector, $\tau_C(q)$ is the combined phonon relaxation time, $C_{ph}(q)$ is the specific heat. I assume that in the experiment, the heat flux is in-plane direction along axis x and $V_G cos\phi = V_{G,x}$. The lattice thermal conductivity in the cross-plane (growth) direction z is beyond the scope of this paper. For the isotropic elastic medium $d^3q = 4\pi q^2 dq$ and the formula can be rewritten in Debye approximation as

$$K = \frac{1}{(2\pi)^3} \int V_{G,x}^2 \tau_C(v) C_{ph}(v) \frac{4}{3} \pi q_D^3 D(v) dv,$$

(2)

where $D(v)$ is the phonon density of states (PDOS) introduced as $D(v)dv=4\pi q^2 dq/(4/3\pi q_D^3)$, and q_D is the cut-off wave vector for acoustic phonons related to cut-off frequency v_D through the phonon group velocity. Using the Debye temperature $k_B\theta=hv_D$ (k_B is the Boltzmann's constant), the thermal conductivity reduces to

$$K = \frac{1}{6\pi^2} \left(\frac{k_B\theta}{\hbar} \right)^3 \int \frac{\tau_C(v)}{V_{G,x}(v)} C_{ph}(v) D(v) dv,$$

(3)

where the specific heat is given by

$$C_{ph}(v) = \frac{(hv)^2}{k_B T^2} \frac{\exp(hv/k_B T)}{[\exp(hv/k_B T)-1]^2}.$$

(4)

Although the Debye approximation has been used, the effects of acoustic phonon confinement enter the lattice thermal conductivity of Eq. (3) via decreased phonon group velocity, increased phonon relaxation rate and modified PDOS. The exact PDOS can be calculated numerically using the definition

$$D(v) = \frac{1}{(2\pi)^3} \int \frac{dS_v}{V_G},$$

(5)

where the integral is taken over the area of the surface $v=const$ in q space. The result refers to a single branch of the dispersion relation and unit volume. If one disregards PDOS modification and uses Debye expression $D(v)=3v^2/(v_D)^3$, the thermal conductivity transforms to the familiar form

$$K = \frac{k_B}{2\pi^2} \left(\frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\theta/T} \frac{\tau_C(\xi)}{V_{G,x}(\xi)} \frac{\xi^4 e\xi}{(e^\xi - 1)^2} d\xi,$$

(6)

where $\xi=hv/k_B T$. Here the change in the phonon group velocity due to confinement affects the phonon relaxation rate τ_C. The phonon group velocity that enters Eq. (6) is

averaged over all populated modes using the procedure outlined in Ref. [14]. The combine scattering relaxation time includes all major phonon scattering mechanisms and is given as

$$\frac{1}{\tau_C(v)} = \frac{1}{\tau_U(v)} + \frac{1}{\tau_I(v)} + \frac{1}{\tau_B(v)} + \frac{1}{\tau_e(v)},$$

(7)

where τ_C is the combined phonon relaxation time due to different scattering mechanisms which are dominant in silicon at room temperature and above. Particularly, the mechanisms include Umklapp scattering (τ_U), mass-difference (or isotope) scattering (τ_I), boundary scattering (τ_B), and phonon-electron scattering (τ_e). In order to determine the lattice thermal conductivity, I calculate all phonon relaxation times in a low-dimensional structure taking into account their modification due to spatial confinement of phonon modes. Mass-difference scattering arises due to the presence of atoms with a mass different from the average atomic mass in a semiconductor. Different masses can come from the isotopes of particular elements or impurity atoms. In the latter case, the difference in stiffness constants between the impurity-host atoms and the host-host atoms, as well as the difference in the atomic volume of the impurity atoms should also be included in the phonon scattering rate expression. I use the standard formulae for the mass-difference scattering but introduce the important modifications – group velocity and PDOS dependence on the structure geometry and boundary conditions. Since the scattering rates strongly depend on phonon group velocity, e.g. $\tau_I \sim V_G^3$, one should expect significant change in the thermal conductivity due to the variation of the phonon velocity [1-4].

B. Phonon dispersion in acoustically mismatched low-dimensional structures

In order to evaluate relaxation rates for all the above processes, one should use the actual dispersion relations and group velocities, $v_g = v_g(\omega(q))$, for phonons in a quantum well. The modification of wave vector selection and frequency conservation rules due to the *spatial confinement* should also be taken into account [2]. We have outlined the general procedure of calculating confined acoustic phonon modes in Refs. [2-3]. Details of numerical calculation of confined modes in quantum wells (thin films) together with electron – phonon scattering rates are given by Bannov *at al*. [15] and Stroscio *at al*. [16]. It is illustrative though to show the dependence of the in-plane phonon group velocity on the cross-plane phonon quantization for shear modes in thin films since it can be done analytically. The phonon dispersion relation for shear modes is written as

$$\omega_n = V_T \sqrt{q_{z,n}^2 + q^2} = V_T \sqrt{\left(\frac{\pi n}{W}\right)^2 + q^2},$$

(8)

where $q=q_x$ is the phonon wave vector along in-plane x direction, W is the thin film (quantum well) thickness, V_T is the transverse phonon group velocity in bulk material (transverse sound velocity). The phonon wave vector along the film growth (cross-plane) direction $q_{z,n}$ is quantized in order to satisfy free-surface boundary conditions. The phonon group velocity can be obtained from the above equation, and it is given by

$$V_{G,x} = \frac{d\omega}{dq} = \frac{V_T}{\sqrt{\left(\frac{\pi n}{Wq}\right)^2 + 1}}.$$

(9)

Thus for the lowest phonon mode (n=1) in a quantum well of thickness $W=10a$, and a phonon wave vector close to the Brillouin zone center $q= (1/10)q_B$ the group velocity $V_{G,x} \sim 0.71\ V_T$ (a is the lattice constant and $q_B=\pi/a$ is the zone boundary wave vector). For the second and the third modes the group velocities are $V_{G,x} \sim 0.44\ V_T$ and $V_{G,x} \sim 0.32\ V_T$, respectively. The average over all populated modes gives rather significant drop in the group velocity.

Substitution of the $< V_{G,x}>$ into the expressions for the phonon relaxation rates [1-3] leads to a strong increase of the combined scattering rate (Eq. (7)). One should also mention that analogous modification of the phonon relaxation is achieved for the clamped-surface boundary conditions. The important question to ask now is whether acoustic phonons are indeed confined as predicted by the theory in real low dimensional structures with sharp interface and finite acoustic mismatch between structure material and the surrounding material. Phonon folding in superlattices with small acoustic impedance mismatch (AlGaAs/Al$_x$Ga$_{1-x}$As) is relatively well-researched topic [17]. In such structures, the modification of phonon transport comes from the additional periodicity in the direction of superlattices layering. The phonon modes extend many periods of the superlattice and are not confined to a single layer. The phonon folding leads to formation of minizones and gives rise to mini-Umklapp processes predicted in Ref. [18]. The situation is quit different in single quantum wells embedded into material with distinctively different elastic properties, which is characterized by a large acoustic impedance mismatch. Here the phonon modes are confined (or nearly confined) into a single layer. The phonon dispersion changes due

to spatial quantization induced by the boundaries. Acoustic phonon confinement in single thin films or superlattices with large acoustic mismatch has not been experimentally investigated yet. In the next section I present the results of high-resolution Raman spectroscopy that shed light on confined nature of phonon transport in low dimensional structures.

III. EXPERIMENT

A. Sample preparation and measurements

In order to investigate the nature of acoustic phonons in semiconductor thin films I have chosen to use ultra-thin silicon-on-insulator (SOI) structures. The SOIs have been specially prepared by wafer-bonding technique (BESOI). The details of the preparation have been reported in Ref. [19]. The state-of-the-art technology allowed the fabrication of ultra-thin Si films with thickness W=30 nm, - 90 nm, and very sharp boundaries. The films were embedded within materials of significantly different elastic and crystalline properties such as SiO_2. Thermal conductivity of SiO_2 varies from 0.66 W/mK for BESOI to 1.4 W/mK for bulk fused quartz, as compared to 148 W/mK for bulk Si. The ultra-thin SOI structures are well suited for study of confined phonon thermal transport since the heat flux mostly propagates in the in-plane direction, and the acoustic phonon modes are confined due to nanoscale width.

Small period Si/Ge superlattice structures grown on a p-type Si (100) wafer have also been examined. A detail description of the structure and preparation procedure have been reported by Lui *et al.* [13]. A typical structure consists of a buffer layer, and 150 periods of Si and Ge layers with thickness of 33 Å each. The superlattice has a uniform heavy n-type doping. The samples were grown using a solid source molecular beam epitaxy (MBE) system. After a standard chemical cleaning and thermal cleaning process, the substrate temperature was reduced and kept at 500°C. 1.1μ-thick relaxed $Si_{1-X}Ge_X$ graded buffer was then grown on the substrate. Ge concentration x is ranging from 0 to 1 with a step of 0.1, which means there are 11 layers with each layer thickness of 100 nm in the buffer. On the top of the buffer, there are 150 periods of 33 Å Si /33 Å Ge superlattice with a uniformly heavy n-type doping.

Raman spectra were measured using a Renishaw Raman 2000 microscope at the room temperature. All spectra were excited by the 514-nm line of an Ar ion laser in the back-scattering configuration and recorded by a Si CCD camera. The spectral resolution of the instrument was about 0.1 cm^{-1}.

B. Raman spectra of ultra-thin SOI structures

A typical spectrum of SOI structure with 30 nm tick Si layer is shown in Figure 1. In addition to easily recognizable Si peaks at 522 cm^{-1} (TO), 970 cm^{-1} (2TO), 434 cm^{-1} (LO), and 302 cm^{-1} (2TA/LA), I have also observed quasi-equidistant peaks in the low-frequency end of the spectrum, in the range from 50 cm^{-1} to 160 cm^{-1}. The peaks below 50 cm^{-1} have been cut by the Raman spectrometer filter. Vanin *et. al.* [20] reported an observation of a set of intense, narrow and equidistant peaks at wave number of 25, 50 and 75 cm^{-1} that were attributed to nanocrystalline silicon dioxide. In order to exclude similar types of local vibrational modes of SiO_2 from consideration, I have carried out Raman spectroscopy of Si substrates with the layers of SiO_2. In this case, no peaks were observed in the specified frequency range from 50 cm^{-1} to 160 cm^{-1}. The investigation was performed for different samples to make sure that the presence or absence of peaks is not related to the finite penetration depth of the incident laser light. The spectral position of the additional low-frequency peaks depended on the thickness of the Si layer embedded within layers of SiO_2. The latter can be considered as a strong argument that the peaks are confined silicon acoustic phonons rather then silicon dioxide peaks.

Figure 2 presents a blow-up of the peaks with the exact wave numbers of the peak position. In Table II I present experimental values of phonon peaks extracted from the Raman spectrum of one of the samples, and a theoretical fit based on a calculated phonon dispersion for share acoustic phonons in Si thin film of given thickness (*W*=30 nm). Due to spatial confinement effects bulk acoustic phonon branches (LA and TA) split into many confined (quantized) phonon modes. There are three basic types of the confined modes: shear (SA); dilatation (DA); and flexural (FA). The theoretical fit presented in Table II is obtained using SA modes alone. The energies of these modes have been calculated using the method outlined in Ref. [2-3]. If one includes into consideration all other possible modes (DA and FA) even closer fit can be obtained for all expetrimental energy values. A Raman spectrometer probes these modes for the phonon wave vector *q* close to the center of the first Brillouin zone center. As one can see, the calculated values of the peak positions for a 30 nm wide thin film are in good agreement with the measured ones. It is important to notice, that the theoretical fit was obtained with the lowest confined phonon modes (*n*=1-4) that have higher population probabilities. Thus, one may conclude that the observed additional peaks in the low-frequency end of Raman spectra from ultra-thin SOI structures are indeed related to the spatially confined acoustic phonons.

The confined phonon peaks discussed here originate from a single thin film rather than from a superlattice. They are discribed by different dispersion relation [2] and, in this sense, they have different origin from that of folded doublets in Raman spectra of

superlattice structures, which are discribed by Rytov's model [12]. The fact that acoustic phonons are at least partially confined in low-dimensional structures with finite acoustic misfit indicate that the phonon quantization have to be included in the modeling of phonon transport in such structures. The important consequence from this is that the effective in-plane phonon group velocity will be lower in the low-dimensional structure than in the corresponding bulk material [2-3]. The amount of the velocity decrease, and corresponding increase in phonon relaxation rate, can be "phonon engineered" by appropriate change of the film thickness and the acoustic mismatch ζ. of the boundary material.

C. Raman spectra of Si/Ge superlattices

A typical Raman spectrum of the sample A (Si/Ge superlattice with 3.3 nm thick layers of Si and Ge) is shown in Figure 3. In addition to regular Ge-Ge and Si-Ge Raman peaks, the spectrum clearly displays a vibrational mode of the doublet structure with a midfrequency at $\Delta\omega = 129.1$ cm^{-1}. This doublet has been attributed to the longitudinal acoustic folded phonon mode of the order of $m=3$ (m is the folding index). It is interesting to note that the second order peak is not present for this superlattice since it has equal thickness for Si and Ge layers. This follows from the theory of Raman scattering under assumption of the photoelastic mechanism for light scattering [11]. The intensity of Raman scattering from folded acoustic phonons is given as

$$I_m \propto \left[\frac{P_{Si} - P_{Ge}}{m\pi} \right]^2 \sin^2\left(\frac{m\pi d_1}{d_1 + d_2} \right),$$

(10)

where P_{Si} and P_{Ge} are the photoelastic coefficients in corresponding materials, d_1 and d_2 are the thickness of the Si and Ge layers. It can be seen from Eq. (10) that $I_m=0$ for all even peaks when $d_1=d_2$. The lowest folded phonon mode ($m=1$) is not seen because it is too close to the laser fundamental peak, and thus it is cut by the filter. The higher order peaks are overshadowed by Ge-Ge Raman peak. The assignment of acoustic folded phonon peaks is based on the elastic continuum approximation.

In Figure 4 I present a Raman spectrum of the sample B, which is similar to the sample A but the Ge layer is substituted with $Si_{0.7}Ge_{0.3}$ layer. Since the effective group velocity is higher in this structure, the third order confined peak is shifted toward higher wave numbers. The folded acoustic phonon peak is seen at 152.2 cm^{-1}. This peak is broader than the one in Figure 4. This is attributed to the difference in sample quality, and confirmed by TEM data. The acoustic mismatch for this structure is obviously smaller that for the sample A. The latter may also affect the sharpness of the

observed peak. Knowing the folded peak frequency ω_m and folding index *m*, one can determine the effective phonon velocity from Rytov's model $V_{eff}=\omega_m D/(2\pi m)$. The smallest velocity V_{eff}=1.5 x 10^5 cm/sec, which is much less then expected from the bulk values, has been obtained for Si/Ge superlattice with 150 periods of 33 Å wide Si and 33 Å wide Ge layers. This shows that Si/Ge superlattices specifically designed for thermoelectric applications have the acoustic impedance mismatch, which is large enough in order to modify phonon transport in such structures, and introduce folded phonon mini-zones [11].

IV. NUMERICAL RESULTS AND DISCUSSION

The results of high-resolution Raman spectroscopy indicate the presence of confined acoustic phonons in single Si quantum wells embedded into acoustically mismatched material (ultra-thin SOI). The Raman spectra of Si/Ge superlattices, designed for thermoelectric applications, with acoustic mismatch between Si and Ge layers of about 0.71 have also shown folded acoustic phonons. This means that an accurate description of phonon transport in such structures and calculating of the lattice thermal conductivity are to take into account modification of the acoustic phonon modes. A simple way of including the effects of phonon confinement into consideration has been outlined in section II.

First, we calculate phonon dispersion in a low-dimensional structure with given geometry and boundary conditions. Large acoustic impedance mismatch ζ allows to approximate the boundaries of the structure with either free-surface or clamped surface conditions. The in-plane phonon group velocity is then found by numeric differentiation for each phonon branch separately. The averaging of the group velocity takes into account the population factor and is carried out using the procedure outlined in Ref. [14, 21, 22]. Based on averaged values of the phonon group velocity, one calculates the phonon density of states (PDOS) in the given structure and the combined phonon relaxation rate. One should note here that in our previous calculations we did not take into account modification of the PDOS and used Debye PDOS. As an example, I calculated the phonon density of states for a 15 nm wide Si quantum well (see Figure 5). The low-energy part of PDOS is similar to Debye density of states proportional to the square of the phonon energy (frequency). Narrow peaks around 5 meV that go to infinity are associated with the onset of the second and third confined acoustic (DA) phonon branches. At the maxima of these peaks the phonon group velocity is zero. Thus, the weighted contribution of the phonons with these energies (frequencies) $<V_G(v)>^2 D(v)$ does not go to infinity. The contribution of the high-energy phonons in the low-dimensional structures is cut due to the modification of the PDOS as compared to bulk described by Debye density of states. This behavior of the PDOS is somewhat analogous to the one reported for binary skutterudites [23]

with the weighted PDOS dominated by the low frequency part of the phonon spectrum (below 100 cm^{-1}).

The phonon scattering rates have been evaluated for a bulk silicon slab (10 μm thick) and a silicon quantum well (W=15 nm). The material parameters used in simulation were the following: the lattice parameter a=5.45 A, density ρ=2.42 x 10^3 kg/m^3, mass of an atom M=46.6 x 10^{-27} kg, the number of atoms per unit cell n$_a$ ~ 7.3, Gruneisen parameter γ=0.56, θ=625 K, and the isotope factor Γ x 10^4 = 2.64 for three Si isotopes. In the case of bulk material, the U-process is a dominant scattering mechanism over almost the entire relevant phonon frequency range. The latter is expected at room temperature and above. The scattering rate due to boundaries is two orders of magnitude smaller then intrinsic scattering rates for a given slab thickness. For the quantum well, the impurity scattering rate, which is proportional to ω^4 is the dominant process at high phonon frequencies. The dominant mechanism at low phonon frequencies is the boundary scattering. The overall scattering rate increases in a quantum well. One important thing to note is that by improving crystal and surface quality one can reduce the impurity and boundary scattering rates but not the Umklapp scattering rate. The increase of the U-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 [2,3].

Knowing $V_{G,x}(v)$, $\tau_C(v)$, and $D(v)$ we can evaluate the in-plane lattice thermal conductivity K for the quantum well (thin film embedded into material with large acoustic mismatch) using Eq. (3). If Debye PDOS is used like in our earlier model [2], one can calculate K from Eq. (6). Figure 6 shows the calculated in-plane lattice thermal conductivity as a function of the absolute temperature. For comparison the results are presented for a bulk slab and the 15 nm quantum well (thin film) with clamped surface boundaries. Two curves for each case correspond to calculations carried out for thermal conductivity limited by the three-phonon Umklapp scattering only, and by all resistive scattering processes combined. Note a strong decrease of the lattice thermal conductivity due to acoustic phonon confinement in low-dimensional structures with finite acoustic mismatch.

The conclusion about significant decrease of the in-plane lattice thermal conductivity in low-dimensional structures with finite acoustic mismatch agrees well with available experimental data. Borca-Tasciuc *et al*. [24] reported measurements of the thermal conductivity for similar Si/Ge superlattice structures described in section II. The measurements have been carried out using the 2 wire-3ω method. The measured thermal conductivity of the superlattice of the sample with the period of about 3 nm was 1.7 W/mK in the in-plane direction and 2.78 W/mK in the cross-plane direction [24, 13]. Obtained thermal conductivities were considerably lower than those determined using the bulk thermal conductivities for Si, Ge, and Si$_x$Ge$_{1-x}$ alloys. The strongest drop in thermal conductivity corresponded to the lowest phonon group

velocity extracted from the Raman data [13]. The latter could be attributed to the modification of the phonon modes, which manifests itself as phonon folding in the Raman spectra. At the same time, it is still too early to make final conclusions about the strength of the correlation of the phonon mode modification in the acoustically mismatched low-dimensional structures with the drop in the lattice thermal conductivity. This is due to the difficulties in measurements and accurate experimental separation of the in-plane and cross-plane thermal conductivity of ultra-thin films.

The confinement of phonon modes strongly increases phonon relaxation (via scattering on isotopes, impurities, and anharmonic interactions) but does not significantly increase phonon-electron scattering rates [4]. Due to this reason, one can realize "electron transmitting – phonon blocking" transport regime, which leads to *ZT* increase. The results of this investigation show that by changing thickness of semiconductor layers and their acoustic mismatch with the boundaries, we can optimize the thermoelectric properties of low-dimensional structures via phonon engineering.

IV. CONCLUSIONS

It has been shown that strong modification of the phonon dispersion and group velocities in the acoustically mismatched low-dimensional structures leads to a significant increase of the phonon relaxation rates and change of the phonon density of states. As a result of this modification, one can observe a decrease of the in-plane lattice thermal conductivity. A theoretically predicted modification of the acoustic phonon transport has been experimentally confirmed using high-resolution Raman spectroscopy of ultra-thin silicon-on-insulator (SOI) structures and Si/Ge superlattices with small periods. The obtained experimental data indicate multiple confined acoustic phonon peaks in Raman spectra of the SOI structure with the thin film thickness of 30 nm. The Raman spectra of the Si/Ge superlattices manifest folded acoustic phonon doublets that indicate confined nature of phonon transport in such structures. Engineering of phonon modes via selective spatial confinement in acoustically mismatched low-dimensional structures opens up an additional tuning capability for optimizing of the thermoelectric properties of semiconductor structures.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. Raman spectrum of the ultra-thin BESOI structure. The thickness of the silicon layer is W=30 nm. Additional peaks in the range from 50 cm^{-1} to 140 cm^{-1} have been attributed to the confined acoustic phonons.

Figure 2. Low-frequency tail of the Raman spectrum of the ultra-thin BESOI structure. The thickness of the silicon layer is W=30 nm. The exact position of the confined acoustic phonon peaks is indcated. The peaks below 50 cm^{-1} are cut by the Raman spectrometer filter. The peak position changes with the thickness of the Si layer.

Figure 3. Raman spectrum of Si/Ge superlattice designed for thermoelectric applications. A third order folded peak from the longitudinal acoustic phonon is clearly seen at 129.1 cm^{-1}. Note the doublet structure of the peak which is clearly seen for this sample. The acoustic impedance mismatch between Si and Ge is about 0.71.

Figure 4. Raman spectrum of Si/SiGe superlattice. A folded peak from the longitudinal acoustic phonon is seen at 152.2 cm^{-1}.

Figure 5. Phonon density of states (PDOS) calculated for a 15 nm wide Si quantum well. The low-energy part of PDOS is similar to Debye density of states proportional to the square of the phonon energy (frequency). Narrow peaks around 5 meV that go to infinity are associated with the onset of the second and third confined acoustic (DA) phonon branches. At the maxima of these peaks the phonon group velocity is zero. Note that the contribution of the high-energy phonons in the low-dimensional structures is cut due to the modification of the PDOS as compared to bulk described by Debye density of states.

Figure 6. Calculated in-plane lattice thermal conductivity as a function of the absolute temperature. For comparison the results are presented for a bulk slab and a 15 nm thin film (clamped surface boundaries). Two curves for each case correspond to calculations carried out for thermal conductivity limited by the three-phonon Umklapp scattering only, and by all resistive scattering processes combined. Note a strong decrease of the lattice thermal conductivity due to acoustic phonon confinement in low-dimensional structures with finite acoustic mismatch.

	Silicon (Si)	Germanium (Ge)	Si/Ge Mismatch ζ
ρ (kg/m^3)	2330	5323	-
V_L (m/s)	8433	4914	0.75
V_T (m/s)	5845	3542	0.71

Table I. Material parameters of Si and Ge

E^{exp} (1/cm)	58.1	73.4	93.7	117.4	141.1
E^{exp} (meV)	7.2	9.1	11.62	14.56	17.48
E^{th} (meV)	7.2	10.8	-	14.4	18.0
m	2	3	-	4	5

Table II. Theoretical fit of the observed peaks with share phonon modes

MODIFICATION OF THE
PHONON DENSITY OF STATES
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