Optimization of the Thermoelectric Properties of Low-Dimensional Structures via Phonon Engineering


* Electrical Engineering Department, University of California, Riverside, CA 92502
  E-mail: alexb@ee.ucr.edu
  Phone: (909) 787-2351
  FAX: (909) 787-2425

# Device Research Laboratory
Electrical Engineering Department, University of California, Los Angeles, CA 90095
E-mail: ahit@ee.ucla.edu
Phone: (310) 206-7987
FAX: (310) 206-4685

+ Nanoscale Heat Transfer and Thermoelectricity Laboratory
Department of Mechanical and Aerospace Engineering, University of California, Los Angeles, CA 90095
E-mail: gchen@seas.ucla.edu
Phone: (310) 206-7044
FAX: (310) 206-2302

Abstract

We report the first direct observation of confined acoustic phonon modes in a single semiconductor thin film. High-resolution Raman spectroscopy of ultra-thin silicon-on-insulator (SOI) structures reveals multiple quasi-equidistant peaks in the spectral range from 50 cm\(^{-1}\) to 160 cm\(^{-1}\). Confined nature of phonon transport in low-dimensional structures with the finite acoustic mismatch indicates an additional tuning capability for optimizing of thermoelectric properties of these structures. Our experimental results are consistent with the recent theoretical predictions of the strong decrease of the lateral lattice thermal conductivity due to phonon confinement.

Introduction

It has been recently predicted theoretically that confinement of acoustic phonons in semiconductor structures brings about significant modification of their thermoelectric properties [1-3]. The predicted increase of the thermoelectric figure of merit in quantum wells and superlattices with distinct boundaries has been a result of a significant drop of the phonon group velocity due to spatial confinement [3]. The latter leads to an increase of the phonon relaxation rate and thus, to a strong drop of the in-plane lattice thermal conductivity. This modification of the thermoelectric figure of merit ZT comes in addition to earlier predicted increase due to two-dimensional confinement of carriers [4], and increased phonon-boundary scattering in thin-films [5] and in quantum wires [6]. 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 [7]. The effect of boundary resistance on phonon transport was examined in detail in Ref. [8].

Theoretical model developed in Refs. [2-3] 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, which allow for partial phonon wave function penetration through the boundaries. Quantitatively the difference in the “rigidity” of materials can be characterized by the acoustic mismatch $K=\rho_2V_2/\rho_1V_1$, where $\rho_i$ is the density of $i$th material and $V_i$ is its sound velocity. Thus, it is important to establish whether acoustic phonons are indeed confined in a thin semiconductor film embedded within material of finite acoustic mismatch.

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 [9]. These doublets originate due to additional periodicity of the superlattices, and can be theoretically described by Rytov’s model [10]. To the best of our knowledge, spatial confinement of acoustic phonons in Raman spectra of a single thin film has not been demonstrated yet. This is primary due to the lack of high quality thin films with sharp interfaces embedded within material with distinctly different elastic properties. In most of cases, one deals with quantum wells grown on material with very similar crystalline structure.
The effects of phonon confinement on the thermal properties of low-dimensional structures also still await experimental investigation. In this paper we report data indicating confined nature of propagating phonon modes in a single Si quantum well embedded in silicon dioxide. We also establish correlation between the strength of phonon folding in Si/Ge superlattices and their thermoelectric properties.

Sample Preparation and Measurements

In order to prove confined nature of acoustic phonons in semiconductor thin films, we have studied ultra-thin SOI structures specially prepared by wafer-bonding technique (BESOI). The state-of-the-art technology allowed us to fabricate ultra-thin Si films with thickness $W=30$ nm, - 90 nm, and very sharp boundaries (thickness variation $\delta W = 5$ Å). 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 ideal 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.

We have also examined small period Si/Ge superlattice structures grown on a p-type Si (100) wafer. A typical structure consists of a buffer layer, and 150 periods of 33 Å Si / 33 Å Ge superlattice with a uniform heavy n-type doping. Details of the fabrication have been reported elsewhere [11].

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$^{-1}$.

Raman Spectra of Ultra-Thin SOI Structures

A typical spectrum of SOI structure with 30 nm thick 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), we have also observed quasi-equipartition 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.

In order to exclude local vibrational modes of SiO$_2$ from consideration, we 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 quasi-equipartition peaks depended on the thickness of the Si layer embedded within layers of SiO$_2$. Figure 2 presents a blow-up of these peaks with the exact values of the peak position. In Table I we 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 a Si thin film of given thickness [2]. Due to spatial confinement effects bulk acoustic phonon branches (LA and TA) split into many confined (quantized) phonon modes [2-3]. The calculated dispersion relations for thin Si film are shown in Figure 3. Raman spectrometer probes these modes for the phonon wave vector $q$ close to the center of the first Brillouin zone center.

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.

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.

Figure 2. Low-frequency tail of the Raman spectrum of the ultra-thin BESOI. The peaks below 50 cm$^{-1}$ are cut by the Raman spectrometer filter. The peak position changes with the thickness of the Si layer.

Thus, we may conclude that the observed additional peaks in the low-frequency end of Raman spectra from ultra-thin
SOI structures are indeed related to spatially confined acoustic phonon modes. These confined phonon peaks originate from a single thin film rather than from a superlattice. They are described by different dispersion relation [2] and, in this sense, they have different origin from that of folded doublets in Raman spectra of superlattice structures [9] which are described by Rytov’s model [10].

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<th>$E^{exp}$, meV</th>
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<tr>
<td>$E^{theo}$, meV</td>
<td>1.1</td>
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The fact that acoustic phonons are at least partially confined in low-dimensional structures with finite acoustic mismatch 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 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 acoustic mismatch $K$ of the boundary material.

### Thermal Conductivity of Si/Ge Superlattices

Phonon quantization observed in Raman spectra of ultra-thin SOI structures with sharp boundaries should have strong effect on thermal transport in these structures. The measurement of the in-plane thermal conductivity of SOI structures is currently in progress.

![Figure 3. Confined dilatational acoustic phonon modes in a 10 nm wide thin Si film. For comparison, the dashed line shows the bulk dispersion. Note that the slopes of the phonon dispersion branches, which define the group velocity, are smaller in the thin film than in the bulk.](image)

This work is significantly complicated by the very small thickness of the Si layers. The smallest SOI structure, for which the in-plane thermal conductivity data was reported [12], had a thickness on the order of 100 nm. It was found that phonon-interface scattering reduces the thermal conductivity by up to 50% at room temperature. We expect that our measurements with 60 nm and 30 nm BESOI will reveal even further decrease due to increased phonon-boundary scattering and confinement of phonon modes.

As an intermediate step, we have measured thermal conductivity of Si/Ge superlattices. This allowed us to examine a correlation between modification of phonon modes in low-dimensional structures and their thermal properties. The acoustic mismatch between Si and Ge is about $K=0.75$. Thus, we can expect that changing thickness of Si and Ge layers and mole fraction in mixed Si$_x$Ge$_{1-x}$ layers, one can re-engineer phonon propagation characteristics in a rather wide range.

Details of Raman spectroscopic investigation of SiGe superlattices with different period $D$ have been reported by us earlier [11]. Knowing the folded peak frequency $\omega_p$ and folding index $m$, we can determine the effective phonon velocity from Rytov’s model $V_{eff}=\omega_p/\nu(2m)$ [10]. The smallest velocity $V_{eff}=1.5 \times 10^5$ cm/sec, which is much less than expected from the bulk values, has been obtained for Si/Ge superlattice with 150 periods of 33 Å Si /33 Å Ge layers.

Thermal conductivity measurements have been carried out using the 2 wire-3o method. The experimental set-up and sample preparation are described elsewhere [13]. The measured thermal conductivity of the superlattice of the sample with $D=3$ nm was 1.8 W/mK in the cross-plane direction. The cross-plane thermal conductivity of the buffer layer was determined to be 7.5 W/mK. Obtained thermal conductivities were considerably lower than those determined using the bulk thermal conductivities for Si, Ge, and Si$_x$Ge$_{1-x}$ alloys [13]. The strongest drop in thermal conductivity corresponded to the lowest phonon group velocity, and could be attributed to the modification of the phonon modes, which manifests itself as phonon folding in the Raman spectra. Currently we are measuring the in-plane thermal conductivity of Si/Ge superlattices using 2 wire-3o method.

Confinement of phonon modes strongly increases phonon relaxation (via scattering on isotopes, impurities, and inharmonic interactions) but does not significantly increase phonon-electron scattering rates [2-3]. Due to this reason, one can realize "electron transmitting - phonon blocking" transport regime, which leads to ZT increase. The results of our 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.

### Conclusions

We have demonstrated confined nature of acoustic phonon modes in a single semiconductor quantum well by carrying out high-resolution Raman spectroscopy of ultra-thin silicon-on-insulator (SOI) structures. The obtained data indicate multiple confined acoustic phonon peaks in Raman spectra of the SOI structure with the thin film thickness of 30 nm. It was also shown that position of the folded doublets...
from the longitudinal acoustic phonons in SiGe superlattices indicates the strength of phonon confinement in these structures and correlates with their in-plane lattice thermal conductivity. Our experimental results are consistent with the recent theoretical predictions of strong decrease of the lateral lattice thermal conductivity due to phonon confinement. Engineering of phonon modes via selective spatial confinement opens up an additional tuning capability for optimizing of the thermoelectric properties of semiconductor structures.

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References


