EFFECTS OF CONFINEMENT AND SURFACE RECONSTRUCTION ON THE LATTICE DYNAMICS AND THERMAL TRANSPORT PROPERTIES OF THIN FILMS

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ABSTRACT
Phonon transport in argon and silicon thin films is examined using harmonic lattice dynamics theory and the Lennard-Jones and Stillinger-Weber potentials. Film thicknesses ranging from 0.8 to 33.5 nm for argon and 0.4 to 8.6 nm for silicon are examined at a temperature of 0 K. Both reconstructed films and films built using the bulk unit cell are considered. Phonon dispersion curves for the in-plane direction and the density of states are computed from lattice dynamics and compared to predictions for a bulk system. The results from the lattice dynamics calculations are used to predict the thermal conductivities of the bulk and thin film structures.

NOMENCLATURE

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<tr>
<td>$c$</td>
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<tr>
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<td>$h$</td>
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<td>$\lambda, \gamma$</td>
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Subscripts

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<td>o</td>
<td>equilibrium position</td>
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<td>SW</td>
<td>Stillinger-Weber</td>
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INTRODUCTION

Advancements in electronics manufacturing techniques have pushed devices into the realm where their thermal properties are both material and geometry dependent. One structure of particular interest is silicon thin films due to their use in transistors [1, 2]. Both phonon confinement and atomic reconstruction at the free surface of the film change the nature of the atomic vibrations compared to bulk behavior. Recent experimental [3, 4] and numerical [5–7] studies have measured/predicted the thermal conductivity of thin films. The thickness of these films is on the order of or smaller than the bulk phonon mean free path, such that the phonon transport will have both diffusive and ballistic character. The film surfaces limit the distance that phonons can move in the out-of-plane direction, reducing the mean free path. At small film thicknesses the phonons interact with the surfaces more than with other phonons. Because of this phonon confinement, the surfaces play a vital role in heat transfer, making thermal conductivity a geometry dependent property. Lattice dynamics calculations have previously been used to examine how the confinement affects the phonon dynamics in silicon thin films [8]. That study, though, neglected the effects of surface reconstruction. Experiments, ab initio calculations, and molecular dynamics simulations have all shown that silicon atoms on a free surface do not remain in a bulk-like configuration, but rearrange themselves into dimers [9–11].

In this work lattice dynamics calculations are used to examine how phonon dynamics in relaxed thin film structures differs from that in bulk materials and thin films with bulk-like structures. Two different materials are considered: argon and silicon. Argon is well suited for initial, exploratory studies. Argon does not lend itself to real world applications; therefore, silicon is also examined. The phonon dispersion relations and density of states are calculated for each material at a temperature of 0 K and at film thicknesses ranging from 0.8 to 33.5 nm for argon and 0.4 to 8.6 nm for silicon. The phonon characteristics of the very thin bulk-like films (BLF) and reconstructed films (RF) are found to differ from each other and from bulk. As the film thickness increases, though, the thin film phonons exhibit bulk traits.

BACKGROUND

Lattice Dynamics

The lattice dynamics method is a technique for computing the natural frequencies of vibration of a crystal structure. The total potential energy of atom \( i \), \( \Phi_i \), is expressed as a Taylor series as

\[
\Phi_i = \Phi_{i,o} + \left. \frac{\partial \Phi_i}{\partial \mathbf{u}_i} \right|_{\mathbf{u}_i = 0} \mathbf{u}_i + \sum_j \left. \frac{\partial^2 \Phi_i}{\partial \mathbf{u}_i \partial \mathbf{u}_j} \right|_{\mathbf{u}_i = 0} \mathbf{u}_i \mathbf{u}_j + \ldots, \tag{1}
\]

where the derivatives are evaluated at the atomic equilibrium positions (denoted by the subscript \( o \)) and \( \mathbf{u}_i \) is the displacement vector of atom \( i \) from its equilibrium position. Under the harmonic approximation the series is truncated after the second-order term. Equation (1) can be further simplified by noting that the first derivative of the potential is the negative of the force on that atom, which is zero at equilibrium. The equation of motion for each atom in the system is given by Newton’s second law as

\[
m_i \ddot{\mathbf{u}}_i = -\sum_j \frac{\partial^2 \Phi_i}{\partial \mathbf{u}_i \partial \mathbf{u}_j} \mathbf{u}_j, \tag{2}
\]

where \( m_i \) is the mass of atom \( i \). The number of equations required to describe the atomic motion can be reduced to a single set of basis atoms that are periodic in the crystal.

Assuming that the solution to Eq. (2) takes the form of a summation of traveling waves, \( \mathbf{u}_i = \sum_k \mathbf{u}_i \exp[i(\mathbf{k} \cdot \mathbf{r}_i - \omega_o t)] \), where \( \mathbf{c} \) is a constant vector, \( i \) is the imaginary number, \( \mathbf{k} \) is the wave vector, \( \nu \) is the dispersion branch, and \( \omega \) is the wave frequency, Eq. (2) becomes

\[
-\omega(\mathbf{k}, \nu)^2 m_i \sum_j \frac{\partial^2 \Phi_i}{\partial \mathbf{u}_i \partial \mathbf{u}_j} \exp[i(\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i))]. \tag{3}
\]

The set of Eq. (3) for all atoms in the basis describes a system of equations that are general and valid for any interatomic potential. The system is an eigenvalue problem where the eigenvalues are the squares of the natural frequencies of atomic vibration and the eigenvectors are the vibrational modes of the basis. The frequencies, \( \omega(\mathbf{k}, \nu) \), are the phonon frequencies and are a function of the wave vector and dispersion branch.

The number of frequencies produced by solving Eq. 3 at a particular wave vector for a three dimensional system, is three times the number of atoms in the basis. Each of these frequencies belongs to a different dispersion branch and can be identified by its eigenvector. The phonon density of states can be found by constructing a histogram from the phonon frequencies calculated at a large number of wave vectors evenly distributed in the Brillouin zone.

Interatomic Potentials

The interactions between argon atoms is modeled with the well-studied Lennard-Jones pair potential [12, 13]. The potential energy between pairs of atoms \( i \) and \( j \) separated by a distance \( r_{ij} \) is given by

\[
\phi_{ij}(r_{ij}) = 4\varepsilon_{LJ}[(\sigma_{LJ}/r_{ij})^{12} - (\sigma_{LJ}/r_{ij})^6]. \tag{4}
\]

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In the case of argon $e_{12} = 1.67 \times 10^{-21}$ J and $\sigma_{12} = 3.40 \times 10^{-10}$ m [14]. In this work a cutoff of 2.5 is used, beyond which the potential is taken to be zero.

The Stillinger-Weber potential is used for silicon [5, 15]. This potential consists of two- and three-body interactions. The two-body term gives the energy between atoms $i$ and $j$ as

$$\Phi_i = \frac{1}{2} \sum_{j \neq i} \phi_{ij}(\hat{r}_{ij}) + \frac{1}{6} \sum_{j \neq k \neq l \neq i} \phi_{ijk}(\hat{r}_{ijk}).$$

(5)

The two body term gives the energy due to the interaction between the triplet of atoms $i$, $j$, and $k$ and takes the form

$$\phi_{ijk}(\hat{r}_{ij}, \hat{r}_{ik}, \hat{r}_{jk}) = \epsilon_{SW}(B\hat{r}_{ij}^p - \hat{r}_{ij}^q) \exp[\gamma(\hat{r}_{ij} - a)^{-1}],$$

(6)

where $\hat{r}_{ij} = r_{ij}/\sigma_{SW}$. The three body term gives the potential energy due to the interaction between the triplet of atoms $i$, $j$, and $k$ and takes the form

$$h(\hat{r}_{ij}, \hat{r}_{ik}, \hat{r}_{jk}) = \epsilon_{SW} \lambda \exp[\gamma(\hat{r}_{ij} - a)^{-1} + \gamma(\hat{r}_{ik} - a)^{-1}][\cos \theta_{ijk} + 1/3]^2,$$

(7)

and $\epsilon_{SW}$, $\sigma_{SW}$, $A$, $B$, $p$, $q$, $a$, $\lambda$, and $\gamma$ are material dependent constants [16]. The constant $a$ is a natural cutoff built into the Stillinger-Weber potential. In the two-body term, $\phi_{ij}(\hat{r}_{ij})$ is set to zero if $\hat{r}_{ij} \geq a$. Likewise if $\hat{r}_{ik} \geq a$ or $\hat{r}_{jk} \geq a$, then $h(\hat{r}_{ij}, \hat{r}_{ik}, \theta_{ijk}) = 0$.

### Atomic Structures

Lattice dynamics is used to study three different configurations: bulk crystal, bulk-like thin film, and relaxed thin film. The bulk lattice is built using the temperature dependent bulk lattice parameter as determined by molecular dynamics (MD) simulations [12]. The crystal is made infinitely large by applying periodic boundaries in all directions [17]. For argon the zero-temperature lattice parameter is 5.27 Å [18]. Molecular dynamics simulations performed using the Stillinger-Weber potential predict a zero-temperature silicon lattice parameter of 5.44 Å. The bulk-like thin films are built in the same manner as the bulk lattice. The only difference is that periodic boundaries are only applied in the $x$-$y$ plane. The top and bottom surfaces of the film are free boundaries, meaning that they experience no external forces. The relaxed thin film structures are determined by performing MD simulations on the bulk-like thin films. The volume of the simulation domain is allowed to change so that the structure remains unstressed. The temperature of the system is reduced from a finite temperature (50 K for argon and 300 K for silicon) to zero by removing a small amount of kinetic energy at each time step. The zero temperature equilibrium positions are taken as the final atomic positions. This quenching process typically occurs over two to three million time steps where each time step is 4.3 fs for argon and 0.38 fs for silicon.

The lattice dynamics method requires that a periodic boundary be defined. In the case of bulk argon this requirement can be met by defining a single atom as the basis and arraying the basis on a face-centered cubic lattice. In the case of the thin films, the crystal is finite in the $z$-direction. Thus the lattice is no longer face-centered cubic and a different basis and lattice must be chosen. The thin film basis used for argon is one that is two atomic layers in each of the $x$- and $y$-directions and extends from the top surface to the bottom surface of the film. The choice of the basis used for the argon thin films is illustrated in Fig. 1. A single block of shaded atoms is arrayed on the lattice to construct the film. The lattice points are defined by the vectors $(l_1 a \hat{a}, l_2 a \hat{b}, 0 \hat{c})$ where $l_1$ and $l_2$ are integers, $a$ is the lattice parameter, and $\hat{a}$, $\hat{b}$, $\hat{c}$ are unit vectors in the $x$-, $y$-, and $z$-directions. The lattice is identical to a cubic lattice in the $x$-$y$ plane. The shortest distinguishable wavelength allowed with this arrangement is $2a$ in the $x$- and $y$-directions. In the first Brillouin zone, the wave vector, $\mathbf{k} = 2\pi/\lambda$, where $\lambda$ is the wavelength, ranges from $-\pi/a$ to $\pi/a$ in both the $x$- and $y$-directions and is zero in the $z$-direction. The $z$-component of the wave vector must be zero since the finiteness of the film only permits the existence of standing waves in the out-of-plane direction.

The basis used for the argon thin film can be used for the bulk-like silicon film but is inappropriate for use with the relaxed film. Silicon atoms on a (001) free surface rearrange themselves to form dimers along the (110) direction as shown in Fig. 2 [9–11]. The dimers destroy the original periodicity of the basis. A new periodic basis can be defined by including eight atomic layers in both the $x$- and $y$-directions. The lattice points can then be defined by the vectors $(2l_1 a \hat{a}, 2l_2 a \hat{b}, 0 \hat{c})$. The larger basis reduces the range of $\mathbf{k}$ to $-\pi/2a$ to $\pi/2a$. The drawback is that this new basis contains four times the number of atoms as the argon basis does for an equivalent number of layers, resulting in more dispersion branches.
Figure 2. SURFACE ATOMS OF THIN FILM SILICON IN (a) BULK-LIKE CONFIGURATION AND (b) RELAXED CONFIGURATION.

Table 1. ZERO-TEMPERATURE IN-PLANE LATTICE PARAMETER FOR ARGON.

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<th>Number of Layers</th>
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</tr>
<tr>
<td>8</td>
<td>5.263</td>
</tr>
<tr>
<td>16</td>
<td>5.270</td>
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<tr>
<td>32</td>
<td>5.270</td>
</tr>
<tr>
<td>64</td>
<td>5.273</td>
</tr>
<tr>
<td>128</td>
<td>5.273</td>
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In order for the phonon dispersion and density of states calculations to be directly comparable between the three configurations the same basis is used in each case. For argon there are two atoms for every atomic layer in the out-of-plane direction resulting in six dispersion branches for each layer. The larger basis used for silicon produces 24 branches per layer. When computing the phonon density of states for the bulk crystal, only wave vectors where the z-component is zero are included, constraining the density of states to the \( k_z = 0 \) plane of the first Brillouin zone. This planar density of states can be directly compared to the density of states for the thin films where the z-component of the wave vector is naturally constrained to zero by the free boundaries. The volumetric density of states and dispersion curves computed from a face-centered cubic basis can be found in references [19] and [20] for argon and silicon.

LATTICE DYNAMICS PREDICTIONS

Argon

Several thicknesses of argon thin films are examined. The smallest film considered is four atomic layers (~0.8nm) thick. Thinner films did not form stable structures. The film thicknesses increase up to a maximum of 128 atomic layers (~33.5nm). The lattice parameters for bulk and the in-plane direction for the relaxed argon films are shown in Table 1. The thinnest film considered has an in-plane lattice parameter that is only 0.26% less than bulk. As the film thickness increases, the bulk parameter is recovered. The out-of-plane lattice parameter is plotted versus reduced atomic position (\( z/(\text{FilmThickness}) \)) for the relaxed argon films in Fig. 3. The plot shows that the atomic layers near the film surface are further apart than the interior atoms. The first two layers on either surface of the films show a significant increase in lattice parameter as compared to bulk. By the third layer, though, the out-of-plane spacing returns to the bulk value.

The phonon dispersion relations are shown in Fig. 4 for bulk argon and both types of argon films with a thickness of four atomic layers. A total of 24 dispersion curves appear in each plot. In the bulk case only 13 curves are distinct, meaning that 22 are two fold degenerate while two of the longitudinal curves are not degenerate. For the thin films there is no degeneracy and all 24 curves are distinguishable. Each of the three plots shown in Fig. 4 is different from the other two, showing that the phonon characteristics in each configuration are different. This can more easily be seen in Fig. 5, which shows that the density of states for each case differ widely. The maximum optical and acoustic phonon frequencies decrease as one moves from bulk to bulk-like film to reconstructed thin film. The dispersion curves also have shallower slopes in the thin film structures indicating a reduced group velocity. This is particularly evident at the boundary of the first Brillouin zone in the reconstructed film. Here, at the reduced wave vector of 0.5 the slopes and therefore the group velocities...
Figure 4. PHONON DISPERSION CURVES IN THE (100) DIRECTION FOR 4 ATOMIC LAYERS OF ARGON ATOMS FOR BULK, BULK-LIKE FILM (BLF), AND RECONSTRUCTED FILM (RF) STRUCTURES.

Figures 4. PHONON DISPERSION CURVES IN THE (100) DIRECTION FOR 4 ATOMIC LAYERS OF ARGON ATOMS FOR BULK, BULK-LIKE FILM (BLF), AND RECONSTRUCTED FILM (RF) STRUCTURES.

Figure 5. PHONON DENSITY OF STATES IN THE $k_z = 0$ PLANE FOR 4 ATOMIC LAYERS OF ARGON ATOMS IN BULK, BULK-LIKE FILM (BLF), AND RECONSTRUCTED FILM (RF).

As the film thickness is increased the phonons approach bulk characteristics. The dispersion curves for bulk and the 128 atomic layer films are shown in Fig. 6. Because there are so many dispersion curves it is nearly impossible to distinguish individual lines, yet, the plots can still be compared. Due to the large number of degenerate dispersion curves in the bulk crystal there are clearly more lines visible in the thin film cases. The regions with high line densities and regions with low line densities correspond between the three plots. The only noticeable exceptions are the two lines that meet outside of the dense region. The phonon density of states for the three configurations, shown in Fig. 7, are nearly indistinguishable from each other, showing that a film of 128 atomic layers of argon reproduces the bulk phonon spectrum.

Silicon
The planar density for states of silicon are shown in Figs. 8 and 9 for four ($\sim 0.5$nm) and 64 ($\sim 8.7$nm) atomic layers. As with argon, the phonon characteristics of the thinnest films are very different from bulk and each other while the thick films exhibit bulk behavior. The dispersion curves (not shown) exhibit the same characteristics as the argon dispersion curves. For the very thin films there are large differences between the phonon distributions of all three configurations. As the film thickness increases the differences between the phonon dispersions become less pronounced.

THERMAL CONDUCTIVITY PREDICTION
The lattice thermal conductivity of insulators is dominated by phonon transport. From kinetic theory the thermal conductivity in the $x$-direction, $k_x$, can be written as [21]

$$k_x = \sum_{\mathbf{k}, \nu} c_{ph}(\mathbf{k}, \nu) v_{g,x}(\mathbf{k}, \nu) \Lambda(\mathbf{k}, \nu),$$

(9)
Figure 6. PHONON DISPERSION CURVES IN THE (100) DIRECTION FOR 128 ATOMIC LAYERS OF ARGON ATOMS FOR BULK-LIKE FILM (BLF), AND RECONSTRUCTED FILM (RF) STRUCTURES.

where $c_{ph}(\kappa, \nu)$, $v_g(x(\kappa, \nu))$, and $\Lambda(x(\kappa, \nu))$ are the phonon specific heat, $x$-direction group velocity, and mean free path. The specific heat and group velocity are readily available from lattice dynamics calculations through the equations

$$c_{ph}(\kappa, \nu) = \frac{\partial}{\partial T} \left[ \frac{\hbar \omega(\kappa, \nu)}{k_B T} \exp\left[\frac{\hbar \omega(\kappa, \nu)}{k_B T}\right] - 1 \right],$$  

(10)

where $\hbar$ is Planck’s constant divided by $2\pi$ and $k_B$ is Boltzmann’s constant, and

$$v_g(x(\kappa, \nu)) = \frac{\partial \omega(\kappa, \nu)}{\partial \kappa_x}.$$  

(11)
The phonon mean free path cannot be directly calculated from harmonic lattice dynamics. Instead, the expression

$$\Lambda(\mathbf{k}, \nu) \propto \frac{a}{a\gamma(\mathbf{k}, \nu)T}.$$  \hspace{1cm} (12)

is used for the mean free path, which applies at high temperature [22]. In Eq. (12) $a$ is the thermal expansion coefficient and $\gamma(\mathbf{k}, \nu)$ is the mode Grüneisen parameter defined as

$$\gamma(\mathbf{k}, \nu) = -\frac{\partial \ln \omega(\mathbf{k}, \nu)}{\partial \ln V},$$  \hspace{1cm} (13)

where $V$ is the crystal volume. The zero temperature phonon frequencies obtained from the lattice dynamics calculations are used when evaluating the thermal conductivity. This represents a simplification since the frequencies are temperature dependent.

Experimental and predicted bulk thermal conductivities of argon and silicon are plotted in Fig. 10. Because Eq. (12) only gives the form of the mean free path and not its magnitude, the thermal conductivities obtained via the lattice dynamics method need to be shifted by a constant value to fit the experimental data. Despite this shortcoming, the method does get the shape of the conductivity curve correct provided that a temperature dependent expansion coefficient is used [23, 24]. The results plotted in Fig. 10 suggest that method described above can be used to estimate the thermal conductivity of argon above 20 K and silicon above 300 K.

For the thin films, instead of the actual thermal conductivity, the ratio of the film to bulk values is computed. If the values of the lattice parameter and expansion coefficient are taken to be the same between the structures then the only parameters the ratio can depend upon are the phonon frequencies and group velocities. The ratios of the reconstructed thin film thermal conductivity to the bulk conductivity for both argon and silicon are shown in Fig. 11. The conductivity of the argon films tends to decrease with increasing thickness (except for the 32 atomic layer film), opposite the expected trend. Not shown are the bulk-like film ratios which tended to be nearly equal to the reconstructed film ratios.

From the silicon thermal conductivity ratios, no clear trend can be established. The thinnest (four atomic layers) and thickest (64 atomic layers) films bound the rest of the data. The results from the remaining three structures lie nearly on top of each other. Also shown in the plot are results from molecular dynamics simulations [27]. It is encouraging that the molecular dynamics results fall in the same region as the results from the lattice dynamics calculations. Contrary to the argon results, the silicon bulk-like film conductivities tended to be several times larger than those of the reconstructed films. The bulk-like film ratios actually follow the expected trend (except for the four atom layer film), increasing toward one with increasing film thickness. The large difference between the bulk-like and reconstructed films is likely due to the large amount of restructuring that occurs at the surface of the relaxed structure.
CONCLUSIONS

The phonon dynamics of bulk crystals, bulk-like thin films, and reconstructed thin films have been examined for both argon and silicon. The phonon dispersion curves and density of states, shown in Figs. 4-9, are obtained through lattice dynamics calculations under the harmonic approximation. The results show that for very thin films even small changes in the positions of the surface atoms have a significant effect on system dynamics. For thick films the surface effects are less important and the bulk phonon characteristics are recovered.

While calculating the lattice thermal conductivity with Eq. (9) predicts the temperature dependence well for bulk systems at high temperatures (Fig. 10), it does not give predictions that are consistent with experiments for the thin films. The trend seen in the argon conductivities is contrary to the expected result and the lack of experimental or other numerical data limits further conclusions. The conductivity results for silicon produced no clear trend.

The anomalous conductivity predictions could have occurred for a number of reasons, which are currently being investigated. First, finite temperature effects could change the qualitative nature of the predictions so that ignoring the effect of temperature on phonon frequencies may be an over simplification. At a finite temperature, the average positions in the bulk crystals are the same as those at zero temperature scaled by a constant, and will reduce the frequency of the phonons but are not expected to alter the shape of the dispersion curves or density of states. At finite temperature the thin films are expected to maintain the same general structures. The films may not expand isotropically as the temperature is increased from zero, resulting in distinctly different phonon dispersion and density of states. Second, while the assumed form of the mean free path appears to work for bulk crystals, it may not be applicable to thin films. The free boundaries present in the thin films give rise to out-of-plane lattice vibrations with very different properties than bulk. For very thin films, phonons cannot develop, only standing waves can exist. For thicker films the phonons that do develop will be limited by the film thickness. It is unclear how these changes in the out-of-plane phonons will affect the phonon-phonon scattering rate.

ACKNOWLEDGMENT

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REFERENCES

[8] Pascual-Gutierrez, J. A., Murthy, J. Y., and Viskanta, R.,


