

Scalability of phononic crystal heterostructures

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Phononic (or acoustic) band structure calculations have been performed for a nanoscale HfO₂-ZrO₂ multilayer stack using first-principles methods at the atomistic level and by solving the acoustic wave equation at the continuum level, as a first step toward determining the length scales when conventional continuum acoustic band-gap treatments become inadequate. Transverse acoustic waves are the focus of this study. The material parameters that continuum acoustic band gap methods require, such as the mass density and transverse wave velocity of the components of the acoustic crystal (i.e., for HfO₂ and ZrO₂), were determined using separate phonon calculations of the corresponding bulk materials. Comparison of the phononic band structure for a nanoscale HfO₂-ZrO₂ multilayer stack calculated using first-principles and continuum methods indicates the need for careful treatments of wave propagation properties at these length scales. © 2005 American Institute of Physics. [DOI: 10.1063/1.2043242]

Acoustic band-gap (ABG) materials^{1,2}—the acoustic analogs of photonic band-gap (PBG) systems^{3,4}—are artificially engineered materials with a spatially periodic variation in the material properties (such as the mass density, elastic moduli, etc.) that determine the propagation of acoustic waves in the medium. Acoustic waves with a half-wavelength of the order of the lattice constant of the ABG crystal undergo Bragg-type wave scattering, and so are forbidden from propagating through such periodic media.

The classical wave equations for both ABG and PBG crystals allow for scaling in the following manner: uniformly expanding or shrinking the physical sizes by a factor α results in the frequency spectrum being scaled by $1/\alpha$.^{1,4} This feature has allowed researchers to indirectly test the properties of ABG and PBG materials at high frequencies (where length scales are small) by studying their scaled analogs at lower frequencies (where the larger length scales allow for easy fabrication).

ABG materials have so far been designed under the assumptions that the properties of each constituent of the crystal are identical to their bulk counterparts, and abruptly change at the interface between the components. It is, however, unclear whether these assumption are valid when system sizes reach nanoscale dimensions, making the applicability of the scaling laws up to nanoscale dimensions rather moot.

In this letter, we address the above questions for the specific case of a one-dimensional heterostructure, composed of ultrathin alternating layers of HfO₂ and ZrO₂, each with a thickness of 5.015 Å. We have computed the phononic band structure of this system using both conventional classical continuum techniques, and using atomistic density functional phonon calculations. The rather extreme choice of thickness of the layers is motivated by the fact that first-principles phonon calculations are very computationally intensive.

The transverse acoustic wave equation in the continuum limit for a solid inhomogeneous along the z direction (but homogeneous along the x and y directions) is given by⁵

$$\rho(z) \frac{\partial^2 u}{\partial t^2} = \frac{\partial}{\partial z} \left\{ \rho(z) c_t(z)^2 \frac{\partial u}{\partial z} \right\}, \quad (1)$$

where $\rho(z)$ and $c_t(z)$ are the position (z component) dependent mass density and transverse wave velocity, respectively, and u is the displacement along the xy plane corresponding to a transverse acoustic wave. Note that for a homogeneous medium for which ρ and c_t are position independent, ρ cancels out, and one is left with the usual wave equation (with a dispersion relation given by $\omega = c_t k$, where k is the wave vector).

Expanding u , ρ , and $\tau (= \rho c_t)$ in a Fourier series, and imposing the Bloch condition on u due to the periodicity along the z direction, one is left with the following eigenvalue problem:

$$\sum_{G'} [\tau(G - G') \cdot (k + G)(k + G') - \omega^2 \rho(G - G')] u_k(G') = 0, \quad (2)$$

which can be solved using standard numerical techniques,⁶ yielding the desired ω versus k relationship (also called the acoustic or phononic band structure). In Eq. (2), G and G' are the one-dimensional reciprocal lattice vectors given by $2n\pi/d$, with n being an integer and d being the lattice spacing of the multilayer structure along the z direction, and k is the wave vector within the first Brillouin zone. Note that $d = d_{\text{HfO}_2} + d_{\text{ZrO}_2}$, the sum of the thicknesses of the HfO₂ and ZrO₂ layers within a repeating unit. Also,

$$\rho(G) = \rho_{\text{HfO}_2} f + \rho_{\text{ZrO}_2} (1 - f), \quad G = 0 \quad (3)$$

$$= (\rho_{\text{HfO}_2} - \rho_{\text{ZrO}_2}) F(G), \quad G \neq 0, \quad (4)$$

where $f = (d_{\text{HfO}_2}/d)$ is the volume fraction of HfO₂, and

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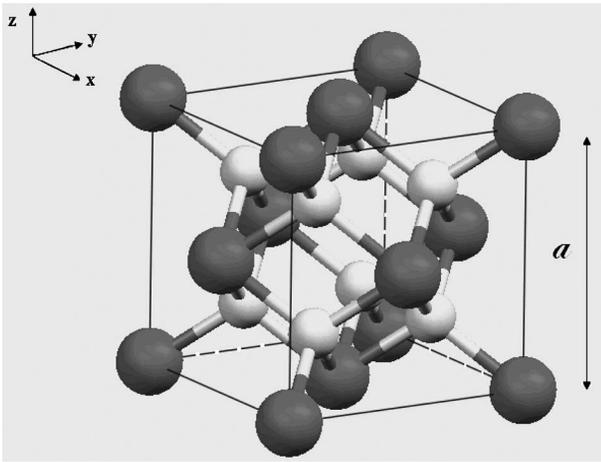


FIG. 1. Structure of the cubic MO_2 ($M=\text{Hf}$ or Zr) unit cell, with a being the lattice constant. White and dark circles represent O and M atoms, respectively. M atoms are at the face center sites of an external cube and O atoms at the simple cubic sites of an internal cube.

$$F(G) = \frac{(\rho_{\text{HfO}_2} - \rho_{\text{ZrO}_2})[\sin(Gd_{\text{HfO}_2}) + i \cos(Gd_{\text{HfO}_2}) - i]}{Gd}, \quad (5)$$

with $i = \sqrt{-1}$. An analogous set of expressions hold for $\tau(G)$ as well.

The values of ρ and c_t in HfO_2 and ZrO_2 are needed to solve for the acoustic band structure of $\text{HfO}_2\text{-ZrO}_2$ multilayer stacks [Eq. (2)]. In the present work, both of these quantities were determined from separate HfO_2 and ZrO_2 phonon calculations using first-principles density functional theory (DFT), within the local density approximation⁷ as implemented in the local orbital SIESTA code.⁸ Phonon calculations were also performed for a $\text{HfO}_2\text{-ZrO}_2$ multilayer stack using this first principles method, to aid in the direct comparison of the phononic band structure calculated using the atomistic and continuum treatments. Norm-conserving nonlocal pseudopotentials of the Troullier–Martins type were used to describe all the elements. The atomic configuration $[\text{Xe} 4f^{14}]5d^2 6s^2$ was used for the Hf pseudopotential, $[\text{Kr}]4d^2 5s^2$ for the Zr pseudopotential, and $[\text{He}]2s^2 2p^4$ for the O pseudopotential. A double-zeta plus polarization basis set was used for all calculations. 75 and 38 special \mathbf{k} points, respectively, yielded well converged bulk (HfO_2 and ZrO_2) and $\text{HfO}_2\text{-ZrO}_2$ multilayer stack results, respectively. The equilibrium positions of the atoms were determined by requiring the forces on each atom to be smaller than $0.04 \text{ eV}/\text{\AA}$.

HfO_2 and ZrO_2 occur in cubic, tetragonal, and monoclinic crystal structures,^{9–11} the simplest of which is the cubic form considered here. Figure 1 shows a schematic of the cubic unit cell. The equilibrium lattice constant of this structure was calculated here to be 5.015 \AA for HfO_2 , which agrees well with prior DFT calculations (5.04 \AA) (Refs. 12 and 13) and experiments (5.08 \AA).⁹ The equilibrium lattice constant for cubic ZrO_2 was calculated here to be 5.02 \AA which too agrees well with prior DFT calculations (5.04 \AA) (Ref. 14) and experiments (5.09 \AA).¹¹

Figure 2 shows the phonon spectra for the cubic bulk phases of HfO_2 and ZrO_2 , both with a lattice constant of 5.015 \AA . The lattice constant of ZrO_2 was constrained at that

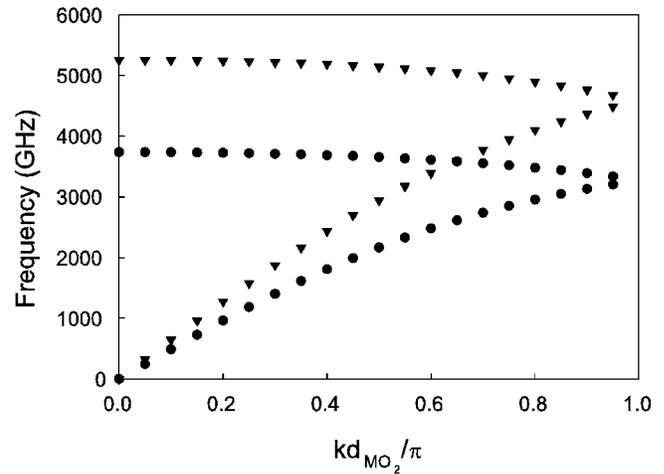


FIG. 2. Phonon spectra along the $(0,0,k)$ direction for cubic HfO_2 (solid circles) and cubic ZrO_2 (solid triangles), with $d_{\text{MO}_2} = 5.015 \text{ \AA}$ ($M=\text{Hf}$ or Zr).

of HfO_2 as ZrO_2 in the multilayer stack was assumed to be lattice matched to HfO_2 . For clarity, only the two lowest-order transverse modes propagating along the z direction are shown. As can be seen, the phonon spectra for the two systems are qualitatively similar. The bulk acoustic velocities of transverse waves in the two systems are given by the slope of the frequency versus wave vector curves at small wave vectors (the continuum limit, where the dispersion relationship is linear, given by $\omega = c_t k$); these are calculated to be 779 m/s and $1,030 \text{ m/s}$, respectively, for HfO_2 and ZrO_2 . The dispersion (or slowing down) of the transverse modes for large wave vectors (which continues after the *zone folding* of the transverse modes at the Brillouin zone boundaries) are atomistic effects that cannot be obtained by standard continuum treatments.

The densities for the two systems can also be determined from their lattice constants and the atomic weights of the constituent atoms; these are determined to be $10,873 \text{ kg/m}^3$ and $6,488 \text{ kg/m}^3$, respectively, for HfO_2 and ZrO_2 . The densities, transverse wave velocities, and the thickness of each layer of the multilayer stacks are the only parameters required to solve for the acoustic band structure of $\text{HfO}_2\text{-ZrO}_2$ multilayer stacks using Eq. (2).

The $\text{HfO}_2\text{-ZrO}_2$ multilayer stack considered here consists of alternating HfO_2 and ZrO_2 layers each one cubic unit cell thick, stacked along the z direction, i.e., with $d_{\text{HfO}_2} = d_{\text{ZrO}_2} = 5.015 \text{ \AA}$. As mentioned earlier, it was assumed that ZrO_2 is lattice matched to HfO_2 . The acoustic band structure for this multilayer heterostructure stack calculated using first-principles methods as well as by using the continuum wave equation [Eq. (2)] is shown in Fig. 3. An acoustic band gap at the Brillouin zone boundary due to Bragg scattering can be seen.

While the spectra calculated using the two approaches are qualitatively the same predicting phononic band gaps that are in reasonable agreement, two important quantitative deviations can be seen: (1) Below the phononic band gap, the slopes of the dispersion relations are different indicating different effective wave velocities. This is presumably because of the extreme situation considered here, namely that each layer of the multilayer stack is just one atomic unit cell thick. In such circumstances, using the bulk properties of each constituent system (that abruptly changes at interfaces) in a con-

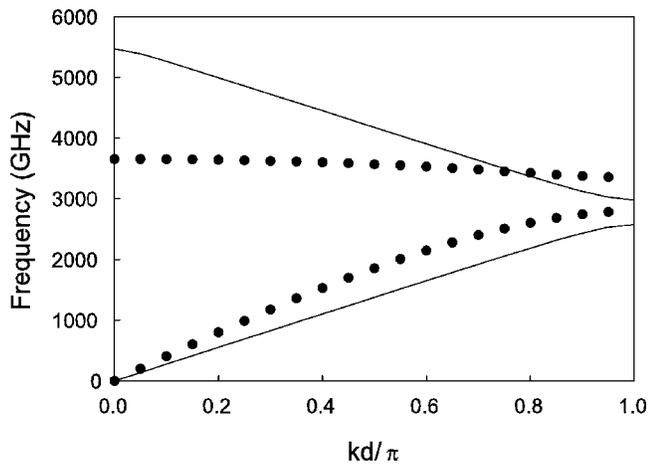


FIG. 3. The phononic band structure of a $\text{HfO}_2\text{-ZrO}_2$ multilayer stack, with $d=2d_{\text{HfO}_2}=2d_{\text{ZrO}_2}=10.030 \text{ \AA}$, calculated using first-principles DFT (solid circles) and by solving the acoustic wave equation [Eq. (2)] in the continuum limit using parameters obtained from first-principles calculations (solid line).

tinuum description of the multilayer is questionable. Also, at the length scales considered here, interface effects due to atom rearrangements become dominant; (2) At frequencies above the phononic band gap, a slowing down of acoustic waves can be seen. This effect was seen in the one-component systems (Fig. 2), and persists in the multilayer stacks as well. Nevertheless, it is expected that as the thickness of each individual layer in $\text{HfO}_2\text{-ZrO}_2$ heterostructures increases to 10 \AA or more, we expect the continuum description to be increasingly valid. This belief is motivated by the fact that atomic rearrangements at interfaces, at least in heterostructures of components with similar crystal structures and lattice constants, is not expected to persist significantly beyond the first atomic layer adjacent to the interface; in fact, ZrO_2 surfaces are known to undergo relatively minor surface relaxations.¹⁵ However, in the case of heterostructures with dissimilar materials, the correspondence between the atomistic and continuum approaches is expected to occur at much

larger thicknesses. In such cases, the interfacial layer can itself be viewed as a third component of the heterostructure, which can in principle allow for realistic continuum treatments of heterostructures even with very thin individual layers.

These results highlight the limits of the continuum description of wave propagation in ordered media, especially the scaling properties, when dimensions approach nanometer-length scales. As ABG devices enter the age of THz frequencies, explicit atomistic treatments using first-principles or semi-empirical methods may become necessary.

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