

Structural and dielectric properties of crystalline and amorphous ZrO_2

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Abstract

We first review earlier work in which we computed the first-principles structural, vibrational, and lattice dielectric properties of the cubic, tetragonal, and monoclinic phases of ZrO_2 and HfO_2 . We then discuss two approaches to the construction of realistic models of amorphous ZrO_2 : a “melt-and-quench” ab-initio molecular dynamics approach, and an “activation–relaxation technique”. The structural, vibrational, and dielectric properties of the resulting models are then analyzed in detail. The overall average dielectric constant is computed and found to be comparable to that of the monoclinic phase. These techniques show promise for future modeling of high-K dielectric ultrathin films and interfaces.

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1. Introduction

The International Technology Road Map for Semiconductors calls for an effective gate-dielectric thickness of approximately 1 nm for 0.1 μm CMOS technology by the year 2006 [1]. In this regime, conventional thermally grown SiO_2 is expected to fail because of issues of tunneling leakage current and reliability. Thus, there are strong incentives to identify so-called “high-K” materials (that is, materials with dielectric constant K , or ϵ , much larger than that of SiO_2 at $\epsilon=3.9$) which could be grown as thicker films while still providing the needed capacitance. A variety of high-K oxides have been proposed, including HfO_2 , ZrO_2 , and their mixtures with SiO_2 .

In this paper, we concentrate on ZrO_2 and HfO_2 . The latter, in particular, is considered to be one of the most promising candidates for replacing SiO_2 in CMOS technology. One of the great advantages of SiO_2 has been the fact that it forms an amorphous oxide (a- SiO_2), thus allowing it to conform to the substrate with enough freedom to eliminate most electrical defects at the interface. ZrO_2 and

HfO_2 can be grown as a metastable amorphous phase on Si using low-temperature deposition techniques. Unfortunately recrystallization tends to occur during subsequent annealing steps that are typically required in current industrial fabrication processes, but it is possible that admixing (alloying) with Si, Al, N, or other chemical constituents may help stabilize the amorphous phase and thereby mitigate this problem [2].

With these motivations, we have embarked on a theoretical study of the structural and dielectric and properties of polymorphic ZrO_2 and HfO_2 crystalline structures, and of amorphous ZrO_2 (a- ZrO_2). Our calculations on crystalline structures indicate that the behavior of ZrO_2 and HfO_2 is generally very similar, so we expect that our work on a- ZrO_2 will be representative of a- HfO_2 as well.

2. Computational technique

The calculations were carried out within state-of-the-art density functional theory (DFT) methods [3] in the local-density approximation (LDA) [4]. Molecular dynamics simulation were carried out with the ab-initio VASP code [5] based on the plane wave formalism with ultrasoft pseudopotentials [6]. The ART [7] technique

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Table 1

Average dielectric constant for three crystalline phases of ZrO_2 and HfO_2

Phase	ZrO_2	Expt.	HfO_2	Expt.
Cubic	37	(35–50) [11]	29	
Tetragonal	47	(35–50) [11]	70	
Monoclinic	20		16	(16–45) [12]

has been implemented in the pseudopotential localized-basis SIESTA code [8], which gives results of similar quality to plane waves at a much smaller computational cost. Technical details can be found in a series of earlier papers [9].

3. Crystalline ZrO_2 and HfO_2

We investigated three crystalline phases of ZrO_2 and HfO_2 : the high temperature stable cubic structure (of CaF_2 type), the tetragonal phase, and the room-temperature stable monoclinic phase. Good agreement was found with experimental structures and zone center lattice vibrational frequencies [9]. The computed Born effective charges and the mode eigenvectors were used to decompose the lattice dielectric susceptibility tensor into contributions arising from individual infrared-active phonon modes.

As shown in Table 1, the static dielectric constant was found to be highly dependent on crystal phase. It is also highly anisotropic for low-symmetry phases, with an especially large dielectric response in the basal plane of the tetragonal structure, as analyzed in our previous publications [9]. The large dielectric constants arise from (i) the presence of relatively low-frequency polar phonon modes, and (ii) “anomalous” (i.e., supernominal) Born effective charges that result from hybridization [10] between O p and cation d states. Our results are consistent with the range of values reported experimentally [11,12].

4. Amorphous ZrO_2

In order to obtain a realistic model of amorphous ZrO_2 , we carried out ab-initio molecular dynamics (MD) simulations of a 96-atom supercell in a melt-and-quench fashion via a series of constant-temperature simulations in which T is sequentially stepped up to about 4000 K, allowing the sample to melt, and then sequentially reduced to room temperature. For each MD simulation, the system is given enough time to thermalize and to eliminate its correlation to the previous structure. We carried out the melt-and-quench procedure in 22 ps of simulation time, 11 ps upon heating and 11 ps upon cooling. The cooling rate (3.4×10^{14} K/s) is far beyond the fastest cooling rate that can be obtained experimentally by laser techniques, as it is limited by the short time interval accessible to simulations. Nevertheless this technique is well accepted and widely

used for the generation of amorphous samples (e.g., for a-Si [13] and a-SiO₂ [14]).

An important issue is the density of the amorphous phase, which, to our knowledge, is not accurately known experimentally. Thus, we performed a series of independent melt-and-quench simulations, each with a different density fixed in the range from 4.34 g/cm³ to 5.96 g/cm³. We found that for densities greater than 5.3 g/cm³ the system recrystallizes upon cooling, supporting the experimental observation of the metastability of a- ZrO_2 at low temperatures. Conversely, we found that for a density as low as 4.34 g/cm³, the system formed a sort of disordered structure with voids and cavities. Among the initial guesses, we found that a density of 4.86 g/cm³ generates a robust amorphous structure, and after careful relaxation of the structure to zero temperature, we analyzed the electronic, structural and dielectric properties of this structure.

The distribution of coordination numbers is shown in Fig. 1, and a snapshot of the system is shown in Fig. 2. A bond cutoff of 3 Å has been chosen for the determination of the coordination number. The average coordination number shows a prevalence of 7- and 6-coordinated Zr over 8-coordinated Zr and of 3-coordinated O over 4-coordinated ones.

Our theoretical amorphous model remains a good insulator with an electronic gap of order ~ 3.4 eV; based on the well-known tendency of DFT-LDA to underestimate gaps, we may expect that the true gap is larger. In any case, the electronic density of states (not shown) indicates that the gap is clean of defect states, despite the amorphous nature of the material and the fairly broad distribution of coordination numbers of the atoms. The electronic contribution to the dielectric constant (ϵ_∞) is similar to that of the crystalline phases, while the Born effective charges (Z^*) are smaller. On average $Z^*(\text{Zr}) = +5.0$ and $Z^*(\text{O}) = -2.5$, compared to average values of $Z^*(\text{Zr}) = +5.4$ and $Z^*(\text{O}) = -2.7$ in the

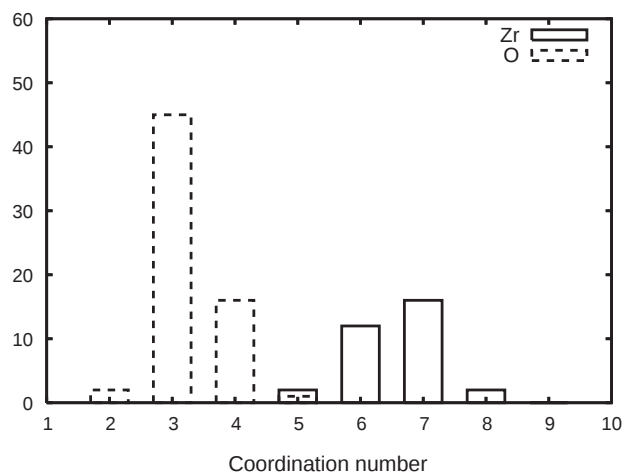


Fig. 1. Distribution of coordination numbers at the end of the “melt-and-quench” MD simulation; Zr and O atoms are indicated by solid and dashed bars, respectively.

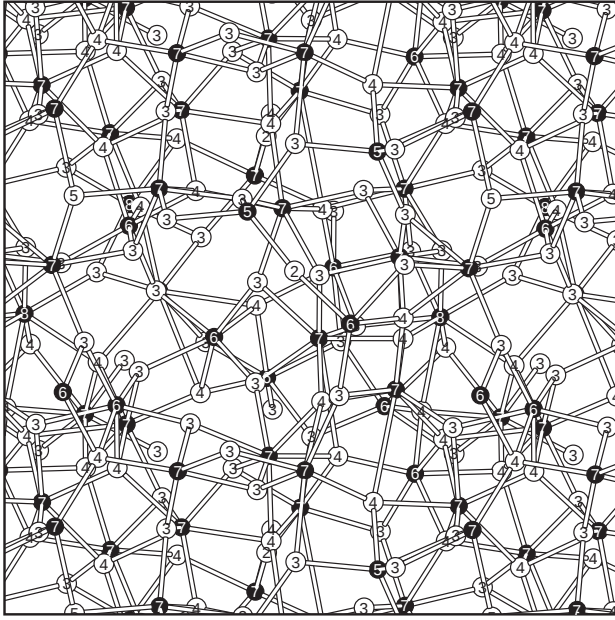


Fig. 2. Structure of amorphous model after “melt-and-quench” MD simulation. Zr atoms are black. O atoms are white. Coordination number is indicated on each atom.

crystalline phases. The dependence of the atomic Born charges on the local environment will be presented elsewhere [15].

We then computed the optical phonon frequencies and eigenvectors, and combined this with the atomic Z^* information to get mode Z^* s and dielectric (infrared) activities. The smaller Born effective charges yield somewhat lower dielectric activities for the phonon modes than in the crystalline phases, and we obtain an overall (orientation-averaged) lattice dielectric constant of $\epsilon_{\text{latt}} = 17.6$. Combining this with our computed orientation-averaged value of the electronic contribution ($\epsilon_{\infty} = 4.6$), we arrive at a value of $\epsilon_0 = 22.2$ for the average dielectric constant of a-ZrO₂.

We also performed a spectral decomposition of the lattice dielectric constant and found that the strongest contributions come from low-frequency phonon modes between about 50 and 200 cm⁻¹, as shown in Fig. 3.

5. Activation–relaxation simulations

In order to see if the fast cooling rate could bias the resulting amorphous structure, we generated an independent amorphous sample by using an event-based structural-evolution approach. Rather than following the irrelevant details of the atomic motions as atoms vibrate back and forth about their average positions for long periods between activated events, the activation–relaxation technique (ART) [7] focuses on simulating jumps over the barriers that separate the different basins of attraction of different local minima in the energy landscape. Thus, it

requires a given computational effort per activated hop instead of per vibrational period. For disordered systems, which tend to show slow evolution, these two time scales may differ by many orders of magnitude, and this event-based technique therefore allows a much faster simulation.

We implemented the ART method in the ab-initio code SIESTA [8]. This code utilizes a localized-orbital basis, allowing the retention of good accuracy in DFT calculations at a strongly reduced computational cost. A single- ζ basis set was optimized [16] in order to reproduce the correct energy order of the cubic, orthorhombic and monoclinic phases of ZrO₂. A cutoff of 150 Ry was used for the expansion of the charge density.

The flowchart of the ART method, as implemented by us, is as follows:

- (1) Start from a local minimum structure.
- (2) (Activation:) Choose one atom at random and displace it in a random direction by a maximum amount of 0.3 Å.

- (a) Perform a conjugate-gradient structural minimization with modified forces

$$\mathbf{g}_i = \mathbf{f}_i - (1 + \alpha)(\mathbf{f}_i \cdot \Delta \hat{\mathbf{r}}_i) \Delta \hat{\mathbf{r}}_i, \quad (1)$$

where the index i runs over all the atoms, $\alpha = 0.15$, and

$$\Delta \mathbf{r}_i = \mathbf{r}_i(\text{actual}) - \mathbf{r}_i(\text{previous local minimum}). \quad (2)$$

- (b) Stop when $(\mathbf{f}_i \cdot \Delta \hat{\mathbf{r}}_i)$ changes sign.

- (c) Cross the barrier: $\mathbf{r}_i = \mathbf{r}_i + 0.05 \Delta \mathbf{r}_i$.

- (3) (Relaxation:) Perform a conjugate-gradient structural minimization with unmodified forces and converge to a new local minimum.
- (4) Compute the energy difference between the new local minimum and the previous one.

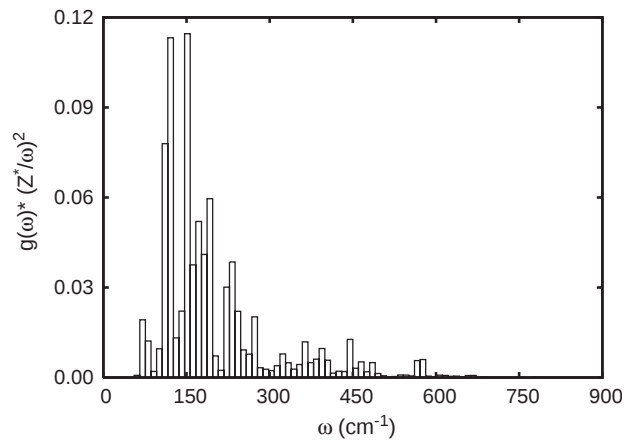


Fig. 3. Infrared activity (i.e., DOS $g(\omega)$ weighted by $\tilde{Z}^{*2}/\omega^2$) of phonon modes in model resulting from “melt-and-quench” MD simulation.

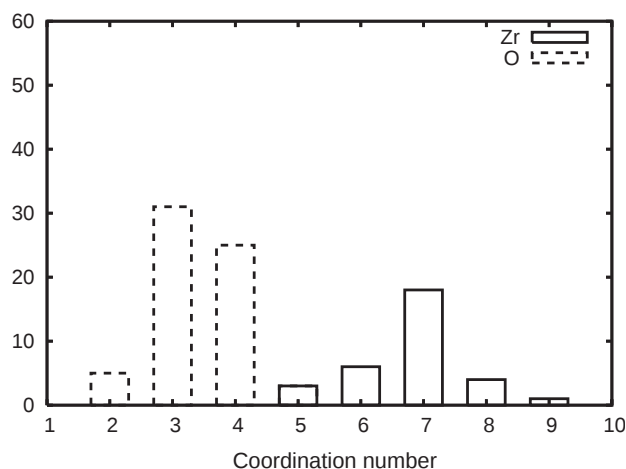


Fig. 4. Distribution of coordination numbers at the end of the activation–relaxation (ART) simulation; Zr and O atoms are indicated by solid and dashed bars, respectively.

- (5) Accept or reject the new configuration according to the Metropolis Monte-Carlo criterion with a fictitious temperature factor β .
- (6) Go back to step 2.

The activation step is based on the physical observation that when the system is deep in the basin of attraction of a local minimum, the restoring force is nearly parallel to the multidimensional vector connecting the actual configuration to the local minimum, Eq. (2). In order to escape from the basin of attraction, the restoring force has to be projected out from the force acting on the system, Eq. (1). This simple procedure causes the system to move towards a saddle point and to sample neighboring local minima efficiently. Step (2c) prevents falling back into the previous basin of attraction.

As reported in [7], we found that a number of Monte-Carlo (MC) trials equal to 5 times the number of atoms (i.e., ~500) was sufficient to produce a good amorphous structure. In our case, an MC temperature of 3000 K produced an acceptance ratio of 0.13. Moreover, we found that during the first 50 MC trials, the acceptance ratio was higher (~0.4) and dropped down in the subsequent trials. We did not attempt to perform longer simulations at a lower MC temperature in order to “anneal” the system further.

The ART simulation was performed at constant volume corresponding to a density of 4.86 g/cm³. A snapshot of the system is essentially indistinguishable, at the visual level, from that of the melt-and-quench MD-generated system of Fig. 2. The corresponding distribution of coordination numbers is shown in Fig. 4. The average coordination number still shows a prevalence of 7- and 6-coordinated Zr over 8-coordinated Zr, but the number of 3- and 4-coordinated oxygens is now nearly the same, as in the monoclinic structure. Furthermore, the calculated phonon spectrum extends over approximately the same range of frequencies (50–800 cm^{−1}) and shows features similar to

those of the sample obtained by melt-and-quench MD simulation. The computed Born effective charges are slightly larger on average, Z^* (Zr)=+5.08 and Z^* (O)=−2.54, but the lattice dielectric constant is 16.5, compared to the value of 17.6 of the MD-generated model, due to the fact that the vibrational spectrum is shifted to slightly higher wavenumbers. Assuming a similar value for the high-frequency dielectric constant (ϵ_∞), the static dielectric constant yields a value of ~21, in good agreement with experimental values and with the previous calculation.

6. Conclusion

In conclusion, we have applied ab-initio electronic structure methods to study the lattice dynamics and dielectric properties of crystalline and amorphous high- K materials. We used both a standard “melt-and-quench” technique and an event-based technique to generate amorphous structures and obtained results of similar quality. The results are in good agreement with the experiment. We note in passing that the ART technique, being an event-driven method, can also be used for studying diffusion processes in solids, and for the generation of amorphous slabs interfaced with crystalline materials.

Acknowledgments

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