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Dielectric properties of nanoscale HfO_2 slabs

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First principles total energy calculations have been performed to determine the extent to which surfaces impact the dielectric properties of ultrathin dielectric materials. HfO_2 (001) slabs in the cubic phase with various thicknesses have been considered in this study. It was found that the induced dipole moment due to an external electric field can be cleanly partitioned into bulk and surface contributions. The bulk part of the dipole moment is linearly related to the slab thickness, and so aids in the accurate determination of the bulk polarization and the dielectric constant. This work has resulted in a simple method for calculating both the electronic and total dielectric constant of a dielectric using standard total energy methods.

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In recent years, dielectric materials of nanoscale dimensions have aroused considerable interest. We mention two examples: (i) in the semiconductor industry, in order to keep pace with Moore's law scaling, the thickness of gate oxide dielectric material is reaching nanoscale dimensions,[1,2] and (ii) the high energy density capacitor industry is currently considering dielectric composites with a polymer host matrix filled with nano-platelets of inorganic dielectric materials.[3–7] Regardless of what the end application may be, it is important to characterize the dielectric properties of materials in the nano-regime, where surface effects naturally play a dominant role.

The primary goal of this work is to determine the extent to which such surface effects modify the polarization, polarizability, and the dielectric constant of systems with one of their dimensions in the nano-regime. Here, owing to its simplicity of structure, we use the cubic phase of HfO_2 as an example system. First principles density functional theory (DFT) based calculations[8] are performed on this system, and the dielectric properties of slabs of HfO_2 are determined by establishing a connection with classical electrostatics.

One of the interesting, and useful, by-products of this work is a simple procedure to determine the electronic as well as the lattice contributions to the bulk dielectric constant. Our procedure is considerably simpler than conventional methods that resort to some form of first order perturbation theory (necessary to determine the electronic contribution to the bulk dielectric constant),[9–11] and laborious phonon and Berry phase calculations (needed to obtain the lattice contribution),[12–14] all within the framework of linear response theory. Treatments that go beyond the linear response framework to determine the dielectric properties of bulk systems have also been performed earlier;[15–17] however, these efforts either involve the minimization of a new energy or free energy functional,[15,16] or involve the imposition of a nonuniform external electric field.[17] The simplicity of our method arises from the fact that most standard DFT implementations can be used as is without the need for additional code development; more importantly, the present approach can treat finite systems such as slabs, with the bulk properties resulting as a by-product. It is worth mentioning that a procedure similar to ours (based on application of an external electric field to slabs) has been suggested earlier to calculate the bulk dielectric constant,[18] but it has been pointed out that this earlier approach has numerical problems preventing a quantitative determination of the dielectric constant.[18] Here we identify potential reasons why this could have been the case in the earlier study.

All calculations were performed using the local density approximation (LDA) within DFT[8] as implemented in the local orbital SIESTA code.[19] Norm-conserving nonlocal pseudopotentials of the Troullier-Martins type were used to describe all the elements. The atomic configuration $[\mathrm{Xe}\ 4f^{14}]5d^26s^2$ was used for the Hf pseudopotential and $[\mathrm{He}]2s^22p^4$ for the O pseudopotential. Semicore corrections were used for Hf. A double-zeta plus polarization (DZP) basis set was used for all calculations. 75 and 32 special **k** points, respectively, yielded well converged bulk and slab HfO_2 results. The equilibrium positions of the atoms were determined by requiring the forces on each atom to be smaller than 0.04 eV/Å.

HfO_2 occurs in cubic, tetragonal, and monoclinic crystal structures,[20,21] the simplest of which is the cubic form considered here. Figure 1 shows a schematic of the cubic HfO_2 unit cell. The equilibrium lattice constant of this structure was calculated here to be 5.015 Å, which agrees well with prior DFT calculations (5.04 Å)[12,22] and experiments (5.08 Å).[20]

Polarization due to an external applied field was studied using supercell slab calculations. In the slab calculations, periodic boundary conditions were applied along the x-y directions parallel to the plane of the slab surfaces. Seven different Hf-terminated slabs were considered, with n cubic units of cubic HfO_2, with $n=1$, 1.5, 2, 2.5, 3, 4, or 5, stacked along the z-direction (referred to henceforth as n-layer slabs). The total dipole moment due to an external electric field of 0.1 V/Å along the z direction was determined both when the atoms were frozen at the field-free equilibrium positions as well as when the atoms were allowed to relax to optimal positions in response to the external electric field.

In supercell calculations involving systems subjected to an external field (or in general in the case of systems that exhibit a dipole moment), the calculated dipole moment is induced due to a combination of the external field and the spurious field due to the periodic image dipoles.[18] In the case

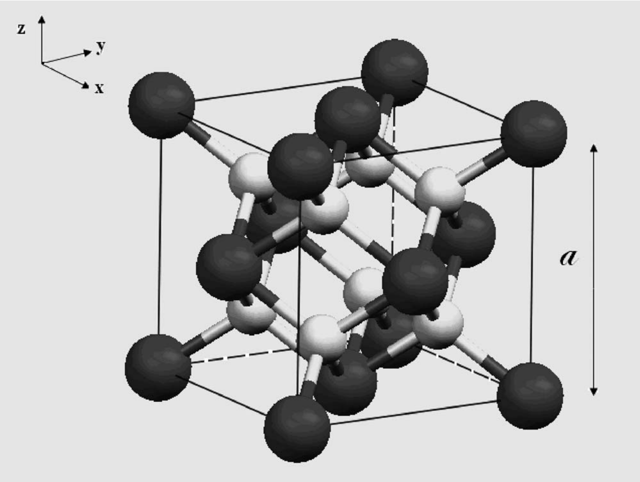

FIG. 1. Structure of the cubic HfO_2 unit cell, with a being the lattice constant. White and black spheres represent O and Hf atoms, respectively. Hf atoms are at the face center sites of an external cube and O atoms at the simple cubic sites of an internal cube.

of slabs, one way of correcting this is by including a term in the Kohn-Sham Hamiltonian representing an additional artificial field that exactly cancels the field due to the image dipole layers.[18] This way, the image correction is included in a self-consistent manner, and the true dipole moment of an isolated slab results.

A second alternative to determining the true dipole moment per unit area, m_0, of an isolated slab (adopted in this work) is to perform the following procedure outside the DFT calculation, with the uncorrected DFT dipole moment per unit area, m, as the starting point. Assume that the *polarizability* per unit area of the slab is α. The dipole moment m is related to the *local* field, E_{loc}, by

$$m = \alpha E_{loc} = \alpha[E_{ext} + m/(L\varepsilon_0)], \tag{1}$$

where L is the supercell height perpendicular to the slab surface. In the above equation, the local field is written as a sum of the applied field, E_{ext} and the field due to the image dipole layers. Recognizing that the true dipole moment per unit area of an isolated slab is given by αE_{ext}, we have (after rearranging terms in the above equation)

$$\frac{1}{m} = \frac{1}{m_0} - \left(\frac{1}{\varepsilon_0 E_{ext}}\right)\frac{1}{L}. \tag{2}$$

Thus the intercept from a plot of the calculated $1/m$ versus $1/L$ will yield the true field induced dipole moment per unit area of an isolated slab. Figure 2 shows a plot of $1/m$ versus $1/L$ for various values of the HfO_2 slab thicknesses, in the presence of an external field of 0.1 V/Å along the slab normal. The atoms were frozen at their field-free positions and were thus not allowed to relax in response to the applied field. The slopes from these plots turn out to be 112.9, 113.4, and 113.6 C/m^2, respectively, for the 1-, 2-, and 3-layer slabs, which compare extremely well with the expected value of 112.9 C/m^2 [calculated as $1/(\varepsilon_0 E_{ext})$], indicating the veracity of Eq. (2). The intercepts of these plots yield m_0 for various slab thicknesses. A similar procedure was adopted to obtain m_0 for all the other cases. Table I lists the calculated field induced dipole moment per unit area for all HfO_2 slabs considered here.

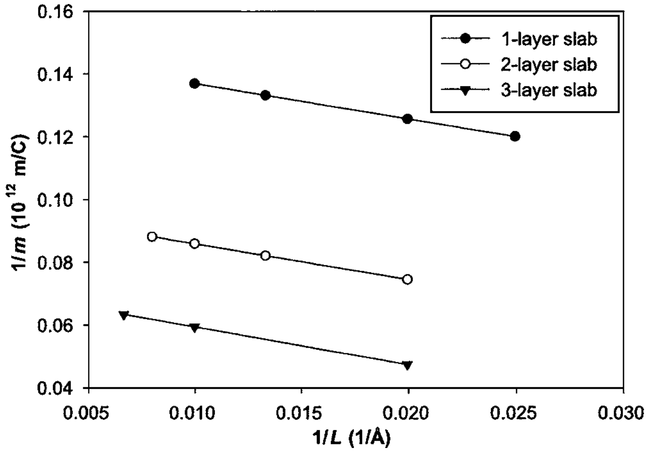

FIG. 2. Dependence of the uncorrected dipole moment of HfO_2 slabs induced by an external electric field of 0.1 V/Å on the supercell height perpendicular to the slab surface.

Figure 3 shows a plot of m_0 versus the slab thickness, both when the atoms were frozen at their field-free positions and when they are allowed to relax to their equilibrium positions. Interestingly, straight line relationships were obtained even for the extremely thin slabs considered here, which can be written as

$$m_0(t) = m_{surf} + \frac{\partial m_0(t)}{\partial t}t, \tag{3}$$

where t is the thickness of the slab, and m_{surf} is the intercept in the m_0 axis. It can thus be seen that the total field induced dipole moment can be partitioned into two parts: one that is independent of the thickness of the slab, viz., the intercept m_{surf}, and so is purely a property of the slab surfaces, and a second part, viz., $m_{bulk}=t\partial m_0/\partial t$, that scales linearly with the slab thickness, indicating that this is a bulk contribution to m_0. The slope, $\partial m_0/\partial t$, is therefore the true bulk polarization, P_{bulk}. In general, P_{bulk} includes both the spontaneous and

TABLE I. The induced dipole moment per unit area of isolated HfO_2 slabs, m_0, due to an external electric field of 0.1 V/Å along the slab surface normal. Atoms were either held fixed at their field-free positions or were allowed to relax to their equilibrium positions in response to the external electric field. Slab thickness is in Å, and m_0 is in 10^{-12} C/m.

Slab thickness, t	m_0 (unrelaxed)	m_0 (relaxed)
5.0150	6.745	6.759
7.5225	8.509	8.907
10.0300	10.29	11.05
12.5375	12.21	13.20
15.0450	14.12	15.40
20.0600	17.99	19.76
25.0750	21.65	23.90

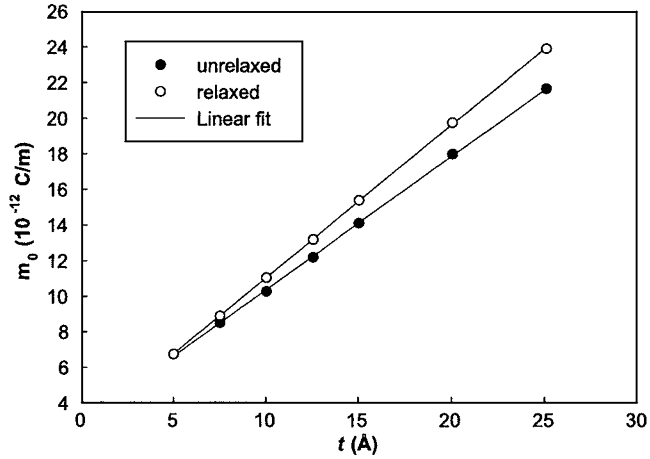

FIG. 3. Dependence of the total dipole moment of an isolated HfO_2 slab on the slab thickness.

electric field induced polarizations, although in the case of cubic HfO_2, it includes just the latter as the former does not exist. Such a partitioning of the dipole moment into surface and bulk contributions is reminiscent of a similar partitioning of the work function discussed elsewhere.[23] It is quite surprising that P_{bulk} can be recovered even from extremely thin slabs; whether this is unique to cubic HfO_2 or is universally prevalent in other dielectrics is currently being investigated.

It can be seen from the values of m_{surf} and P_{bulk} listed in Table II that the surface contribution to the dipole moment can be quite significant especially for the extremely thin (001) films of cubic HfO_2 considered in this work. In general, the ratio of the surface to bulk contributions to the dipole moment is given by $3.9/t$ and $2.9/t$, respectively, for the unrelaxed and relaxed cases, with the thickness t of the slabs in Å. Thus, even for HfO_2 slabs that are about 40 Å, the surface contribution to the total dipole moment can be 7–10%. This is an important result with implications for both the applications mentioned at the outset of this Brief Report: (i) in the gate stack area, the surface dipole moment determines several important interface properties such as band offsets, Fermi level pinning at the interface, etc., and (ii) in situations involving composites with nano-particle or nano-platelet dielectrics embedded in a host matrix, the polarizability, $\alpha[=m_0(t)/E_{ext}]$, of each individual particle is an important parameter in determining the overall dielectric response of the composite. While bonding of the surface atoms to other species—such as metal or semiconductor electrodes, or the host material if the dielectric is used in a composite—will to some extent mitigate or enhance the surface contribution, this analysis underlines the importance of this factor.

TABLE II. Surface and bulk dielectric properties of HfO_2 slabs. m_{surf} and P_{bulk} are the intercept and slope, respectively, from Fig. 3, and are induced due to an external electric field of 0.1 V/Å, applied perpendicular to the slab surfaces. m_{surf} is in $10^{-12\ \mathrm{C/m}}$, P_{bulk} is in 10^{-3} C/m, and t is in Å, ε is the dielectric constant.

	Unrelaxed	Relaxed
m_{surf}	2.88	2.47
P_{bulk}	7.48	8.56
m_{surf}/m_{bulk}	$3.85/t$	$2.88/t$
ε	6.4	30.4
ε (previous work, Ref. 12)	≈5	≈29

The calculated bulk polarization can be used to determine the dielectric constant, ε (also listed in Table II) using

$$\varepsilon = \frac{\varepsilon_0 E_{ext}}{\varepsilon_0 E_{ext} - P_{bulk}}, \tag{4}$$

where ε_0 and E_{ext} are the permittivity of free space and the external electric field, respectively. Using P_{bulk} corresponding to the situation when the atoms were frozen at the field-free position would result in the electronic (or optical) part of the dielectric constant, whereas using P_{bulk} obtained by allowing the atoms to relax to their field induced equilibrium positions would yield the total dielectric constant.

The calculated electronic and total dielectric constants using this method are 6.4 and 30.4, respectively, both of which compare well with prior results. For instance, the electronic part of the dielectric constant determined experimentally as well as calculated earlier using specialized linear response techniques for a general class of dielectrics similar to HfO_2 (although not specifically for cubic HfO_2) is about 5.[9–13] The lattice part of the dielectric constant has been calculated earlier for the specific case of cubic HfO_2, using another specialized linear response theory (that entails the determination of the phonon frequencies[12,13] and Born effective charge tensors,[12–14] both of which are nontrivial computations, in general), and turns out to be 23.9,[12] implying a total dielectric constant of about 29 [note that our calculation yields the lattice contribution to the dielectric constant as 24 (30.4 −6.4), in excellent agreement with the prior calculation].

The advantages of the approach presented here to calculate the dielectric constant include its simplicity (as it involves using standard DFT methods), and the intuitive connection it affords to the conventional classical electrostatic concepts of polarization and dielectric constant. A similar approach (of using slab calculations to determine dielectric properties) has been suggested earlier.[18] In this earlier work, the polarization due to an applied field was calculated as the ratio of the dipole moment per unit area to a suitably defined height of the slab, i.e., as m_0/t', where t' was defined as the distance between the centers of gravity of the screening charge at the top and bottom surfaces of the slab.[18] Presumably, t' should be reasonably close to the thickness of the slab t (defined as the distance between the top and bottom most atoms), especially for thick enough slabs. Regardless of what definition is used for t', one ends up including a term proportional to surface dipole moment density, m_{surf}, in the calculated polarization. This can be seen from Eq. (3); defining an effective polarization, P_{eff} as m_0/t, we have

$$P_{eff}(t) = m_0(t)/t = m_{surf}/t + P_{bulk}. \tag{5}$$

Thus for thick enough slabs, P_{eff} does in fact reduce to P_{bulk}. However, the dielectric constant is very sensitive to the value of the polarization, and so small errors introduced due to the

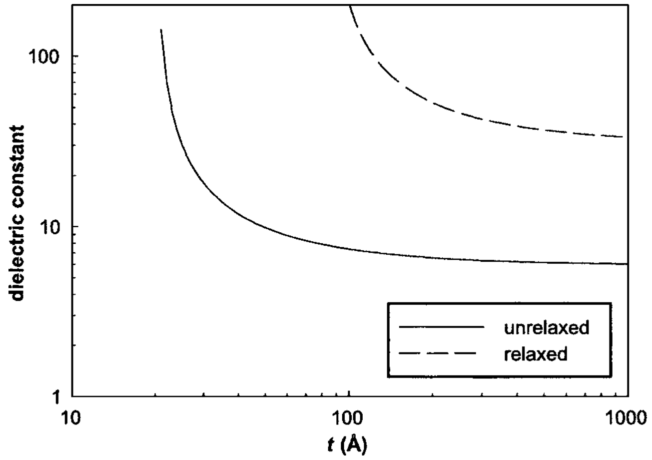

FIG. 4. Dependence of the dielectric constant on the slab size.

inclusion of the undesirable first term in the right-hand side of the above equation (or usage of the wrong t' value as pointed out earlier) can cause large variations in the calculated dielectric constant. To see the magnitude of this variation, we show in Fig. 4 the dielectric constant calculated as a function of thickness t using Eq. (4), but with P_{bulk} in Eq. (4) replaced by P_{eff}. For very small slab thicknesses, P_{eff} can be extremely large, resulting in *negative* values of the dielectric constant. The electronic part of the dielectric constant converges to its bulk value much quicker than the total dielectric constant, owing to its smaller value. In fact, this difficulty, especially for the case when the atomic relaxations are allowed was pointed out in the prior work.[18] The present approach improves on the earlier method by clearly being able to determine the bulk polarization (as the slope of the lines in Fig. 3).

In summary, we have used standard density functional theory based techniques to study the dielectric properties of nanoscale slabs, using cubic HfO_2 as an example system. By establishing a connection between density functional results and conventional classical electrostatics, we were able to partition the total slab dipole moment induced by an external electric field into surface and bulk contributions. The bulk part of the dipole moment is linearly related to the slab thickness, and so aids in the accurate determination of the bulk polarization and the dielectric constant. For cubic HfO_2, this simple procedure yields the electronic (or optical) and total (electronic plus lattice) dielectric constants of 6.4 and 30.4, respectively, in good agreement with earlier calculations based on more involved computational treatments.

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