Anomalous Behavior of the Dielectric Constant of Hafnium Silicates: A First Principles Study

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We present an extensive *ab initio* study of the structural and dielectric properties of hafnium silicates $Hf_xSi_{1-x}O_2$ that accounts for the observed anomalous dependence on composition of the static dielectric constant in the entire x range. The results reveal that this complex behavior reflects that of the structural development with x, from silica to hafnia, and clarify how different growth processes can also lead to scattered sets of data. Several simple models proposed thus far to explain part of the experimental data are shown to be inadequate. It is argued that silicate layers with low hafnium content form at the HfO_2/Si interface and play a crucial role in preserving high electron mobility in the channel.

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In the search for an alternative to SiO_2 as gate dielectric of CMOS devices [1], challenging fundamental issues continue to emerge that are related to the physical properties of the novel candidate oxides, their derivatives, and interfaces. Hafnium dioxide (HfO_2) is the one candidate that seems to better respond to the simultaneous requirements of high permittivity and thermal stability, and that can be integrated in a gate stack with high mobility [2]. However, a microscopic understanding of the ‘‘interaction’’ of the oxide with silicon is still missing. This transpires in all investigations of the interfaces, and is remarkably apparent in the study of hafnium silicates (HfSiO), which have received considerable attention since the pioneering work of Wilk *et al.* [3]. Their interfacial properties with silicon have long been shown to be superior to those of HfO_2 [4], and nitridation has recently been proposed as the means to increase their performance to the point that HfSiON materials were selected for the new generation of low-power MOSFETs [5] and as components of memory devices [6]. However, critical issues are still open, primarily regarding the observed ‘‘odd’’ behavior of their dielectric constant as a function of concentration, their atomic distribution, and their stability against decomposition and segregation, which, as we will show in this Letter, are all interrelated.

The anomalous variation of the dielectric constant ϵ_0 with composition was first pointed out after systematic measurements were made in the entire range from silica to hafnia [7]. It becomes even more intriguing when one realizes that several contradictory experimental data are published for both Si-rich and Hf-rich samples [8]. This odd situation is shown in Fig. 1(a). In particular, earlier measurements indicating that a relatively low content (10%–20%) of either Hf or Zr was sufficient to enhance the dielectric constant of silica from ~4 to ~10 were not confirmed by later experiments [7,8], which also cast doubt on arguments providing an explanation of such an effect [9]. Moreover, a number of controversial results were lately reported regarding the thermal stability of HfSiO thin films grown on a silicon substrate [10], and the formation of silicate interfacial layers after HfO_2 deposition on silicon has been questioned [11].

In this Letter, significant progress is made towards unfolding the above questions on the ground of extensive *ab initio* simulations of the $Hf_xSi_{1-x}O_2$ substitutional alloys and subsequent computations of the dielectric constant performed for the entire range of compositions. The observed anomalous x dependence of ϵ_0 is revealed to be the consequence of major structural changes that the silicates undergo, and the scatter of data produced in different experiments is rationalized. The unprecedented large scale of the structural models studied here enables a more realistic approach, a deeper understanding of these complex materials, and an accurate evaluation of previous simple arguments and paradigms. Moreover, on the basis of our findings we argue that the formation of silicate layers at the HfO_2/Si interface might play a key role in preserving high electron mobility in the channel [12].

Our study relies on density-functional theory (DFT) implemented in the plane-wave-pseudopotential scheme [13], on the harmonic approximation for the vibrational spectra, and on the linear-response theory [14] for the dielectric constant. Beyond the binaries [15,16], a similar scheme has so far been applied only to the midcomposition crystalline compound hafnon [17] and fits well with experimental findings [7,18–22]. Otherwise, only calculations of small clusters are available [23,24] and model approaches to the dielectric properties of the related Zr-silicates [25]. Indeed a reliable simulation of these alloys is challenging because they are generally noncrystalline and a distribution of different local environments is expected on the basis of the vast dissimilarity of coordination (CN) in the component binaries. Moreover, being derived from a limited database referring to CN = 7 or 8 only, the available classical potentials for the description of the Hf(Zr)O and Hf(Zr)Si interactions (see, e.g., [25]) are biased, which precludes the auxiliary use of classical MD. Therefore we adopted the following strategy: (i) several lattices were considered for the initial atomic distributions (six tetragonal, one monoclinic [26]), which were further allowed to

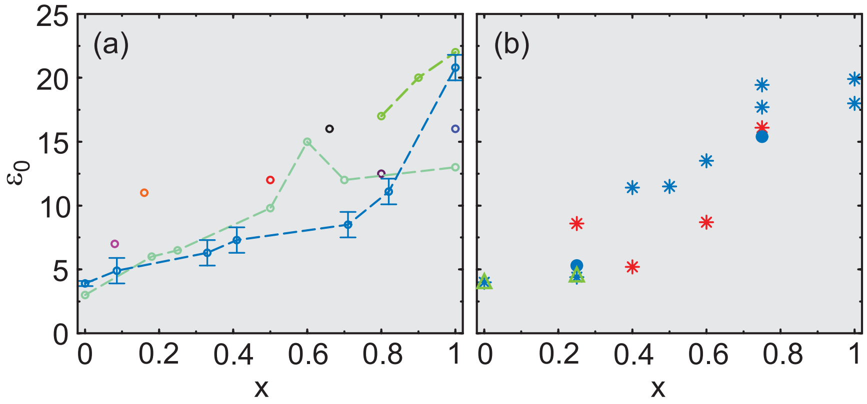

FIG. 1 (color). Dielectric constant vs Hf concentration. (a) Experimental data from Refs. [7] (blue), [18] (turquoise), [21] (green), [8] (magenta), [3(b)] (orange), [19] (red), [10(b)] (black), [32] (brown), and [20] (violet). (b) Our *ab initio* calculations for the thermodynamically favored (blue) and some disfavored structures (red), and "amorphous" silica samples (green triangles) (see text). $*$ stands for configurations with uniform distribution, ● for nonuniform.

both relax and distort so as to minimize the internal stress [26]; (ii) thanks to special implementations of our code for extreme parallel computers [27], such supercells were of an unprecedented large size [324 or 192 (one lattice) atoms], which is crucial for a realistic description of the changes induced by alloying; (iii) in the starting configurations, the minority cations were distributed either randomly or in such a way as to form an agglomerated oxide to mimic internal segregation; (iv) for each of these ~50 samples combined simulated annealing and local optimization techniques were used to let atoms reorganize and lose memory of the initial conditions as much as possible within reasonable annealing schedules [28]; (v) the relative stability was examined on the basis of the relative Helmholtz free energy $\Delta F = \Delta E - T\Delta(S_{\mathrm{vib}} + S_{\mathrm{mix}})$; (vi) in the Si-rich range, we also considered a model of amorphous silica as starting point for the alloy which we obtained using the MD-driven replica exchange method and our newly DFT-derived potentials [29].

A clear trend can be identified in the thermodynamically favored structures. The most salient and unforeseen result is that up to at least $x = 0.25$ Hf atoms do not tend to increase CN above 4 when distributed uniformly over the silica matrix, be it pseudocrystalline or amorphous [see Figs. 2(a) and 2(b)]. The $\widehat{\mathrm{SiOSi}}$ bond-angle distribution [Fig. 2(c)] remains unperturbed, while the $\widehat{\mathrm{SiOHf}}$ one broadens towards smaller values. Our procedure produced also amorphous structures where quasitetrahedral coordinated Si atoms coexist with Hf in higher CN; compared with the silicalike ones, they correspond to a significant density increase and at room temperature ΔF exceeds 0.4 eV. With increasing x they become progressively favored, with a crossover at $x \approx 0.35$. In particular, by offering quasitetrahedral CN to Si and eightfold CN to Hf, hafnon realizes the ideal crystalline intermixing of the two oxides at $x = 0.50$. We find that this basic pattern is still maintained when 10% of the atoms of one cation are replaced by the other, in spite of important changes: at $x = 0.40$ the excess Si atoms rearrange so as to reduce their CN from 8 to 4.6 [average CN(Si) = 4.1], whereas at $x = 0.60$ the average CN(Hf) reduces from 7.4 to ~6.3. While 25% Hf atoms can still be accommodated in the silica network, 25% Si tends to disrupt any hafnia matrix. At $x = 0.75$, all high-CN lattices undergo sizable distortions and strong local atomic reorganization takes place, which invariably yields configurations (spread over 0.1 eV) with predominant HfO_6 distorted octahedra and trigonally distorted SiO_4 tetrahedra, also capped with an additional oxygen (SiO_5) [see Figs. 2(a) and 2(b)]. Note that Hf(Zr)O_6 units are absent in the polytypes of hafnia (zirconia) but characteristic of $(ZrO_2)_x(SiO_2)_{1-x}$ glasses [30].

Given the current time and space limitations, *ab initio* MD experiments are hardly adequate to verify if dissociation takes place. However, a tendency to dissociate was claimed [31] on the basis of ultrashort (at ~1600 K) simulations made on periodically repeated cells of 24 atoms, with parameters fixed to those of hafnon. This does not occur in any of our simulations at least up to ~2000 K on comparable time scales, thus showing the artifact of the previous findings. From ΔF calculations, we find that bulk Hf silicates are thermodynamically unstable against dissociation into the two isolated end-member oxides outside a small window around midcomposition, in which the mixing entropy plays the main stabilizing role. However, configurations in which the minority oxide forms an agglomerate within the matrix of the majority component were not thermodynamically favored with respect to those in which it was uniformly diluted, due to the strong reduction of the enthalpy difference that accompanies the embedding process. At the borders, where the mixing entropy is less effec-

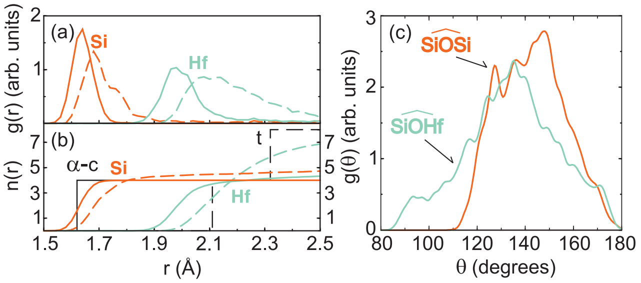

FIG. 2 (color). Radial distribution functions (a) and current CN (b) for $x = 0.25$ (solid) and $x = 0.75$ (dashed). Black lines refer to α-cristobalite (solid) and t-HfO_2 (dashed); bond-angle distribution (c) for $x = 0.25$.

tive, depending on the growth process, internal segregation may coexist in equilibrium with the silicate. Moreover, at the HfO_2/silicon interface, thanks to the stabilizing effect of SiO_2 layers via strain relaxation, silicates may form that have low Hf content and are isostructural with SiO_2.

The complex structural history of these compounds as a function of composition is reflected into dramatic changes of the behavior of $\epsilon_0(x)$, as shown in Fig. 1(b), and also in detectable variations of the optical $\epsilon_\infty(x)$, which, however, cover a much narrower range (from ~2.5 to ~5). In the Si-rich region, the changes relative to the SiO_2 value for ϵ_0 are minimal. Clustering (internal segregation) induces a slight enhancement as shown for $x = 0.25$, as a consequence of a further breaking of symmetry, which affects the coupling of the rocking modes of mixed Si-O-Hf units. This effect provides an explanation for the steady modest increase observed in Refs. [7,18] in the Si-rich regime, but certainly not for the strong enhancement observed in some cases for $x < 0.20$ [8]. Contrary to the arguments of Ref. [9], Hf atoms with CN = 4 do not induce sizable variations of polarizability. On the other hand, unlike the assumptions of Ref. [25], our extensive simulations provide evidence of a substantial presence of HfO_6 units (coexisting with SiO_4 units) only in high-energy high-density disordered structures for which a sizable increase of ϵ_0 is indeed found [see $x = 0.25$ in Fig. 1(b)]. These same comments apply to Zr silicates and are consistent with the unusually low Zr CN (<6) pointed out in early experimental structural studies of glasses of the $(ZrO_2)_x(SiO_2)_{1-x}$ system, at least up to $x = 0.20$ [30]. One could then interpret the anomalously high values measured both for Hf and Zr silicates as a sign of the presence of microdomains, that could enucleate during growth, having local structures other than the silicalike ones.

In the window of stability of the hafnonlike structures ($0.4 \lesssim x \lesssim 0.6$), ϵ_0 is fairly constant around the $x = 0.5$ value (from ~11 to ~13). Lower measurements indicate the presence of silicalike domains [see red symbol in Fig. 1(b) at $x = 0.4$], which can be expected near the border between the two structural regimes. Because of the predominant contribution of the ionic polarizability to ϵ_0, the different polymorphs of hafnia exhibit very different values [18(m), 20(o), 31(c), 41(t)]. In the Hf-rich regime ($x = 0.75$) the tendency of Si to disrupt the host network in a way that is rather independent of the specific HfO_2 matrix, is reflected in a much reduced range of ϵ_0 [Fig. 1(b)]. Internal segregation is more effective here and weakens the dielectric screening via a global depletion of the dipole matrix elements in the 100–300 cm^{-1} region. This mechanism accounts for the behavior observed in Ref. [21], while the much lower values measured in Ref. [7] may signal the presence of silicalike structures that could be stabilized during growth on the (observed) preexisting SiO_2 layers. Indeed, replacing 60% of the Si atoms on a silica matrix makes the structure collapse but results in high-energy ($\Delta F \approx 0.5$ eV) disordered configurations with relatively low density and Si in its typical CN but Hf in 5- (mainly) and sixfold coordination; correspondingly ϵ_0 rises only up to ≈ 8 [see Fig. 1(b)]. On the other hand, the persistence of $\epsilon_0 \approx 12$ in other samples (see, e.g., Refs. [10(b),32]) suggests the formation of hafnon as likely product of internal segregation.

Our *ab initio* results allow us to evaluate the models proposed so far to account for the variation of the dielectric constant of ternary high-*k* dielectrics: (i) We have applied the CN-dependent model of Ref. [25], in which, in analogy with the electronic polarizability, also the lattice term was decomposed into local and additive contributions associated with the different CN units present in the alloy [33]. The effective charges Z^2 and the "inverse force constant" C^{-1} are written as sums over these units with weights given by their relative concentrations. Our calculations reveal that although the former approximation is a good one, the latter is not appropriate and leads to a significant overestimate of the dielectric constant [Fig. 3(a)] in the Hf-rich region. (ii) The important role of atomic CN discounts the validity of simple explanations solely in terms of the atomic density (see Ref. [24]), as dramatically shown in Fig. 3(b). (iii) The virtual crystal approximation [34] offers a reasonable description of the limit of random positional disorder only for $x < 0.3$, namely, in the range where the structure is preserved, and (iv) a stack of silica and hafnia layers with relative thickness proportional to the relative concentration cannot represent the opposite limit of positional order.

In conclusion, the dependence of the static dielectric constant of the HfSiO system on composition is intrinsically nontrivial because of its complex structural evolution, characterized by the tendency of Si to preserve tetrahedral bonding and the versatility of Hf to accommodate to lower CN (4 and 6) than in the crystalline phases. Therefore, this case must be regarded as an outstanding example of the link between atomic structure and dielectric response. The scatter of data measured on different samples can be interpreted consistently with our results and indicates the presence of domains with different local structure, depending on the growth process. In the Si-rich regime ($x < 0.3$), Hf substitution maintains the structure of the silica matrix, and thus has only a minor influence on its vibrational spectrum and dielectric constant. This finding has very important

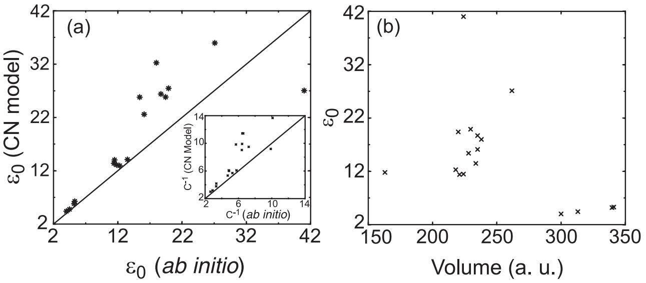

FIG. 3. Dielectric constant: (a) Comparison of our *ab initio* calculations ϵ_0 and the CN-dependent model of Ref. [25]. (b) Missing correlation with the average molecular volume.

implications, because it also indicates that when Hf-silicate layers with low Hf content form at the interface of hafnia with silicon, degradation of the electron mobility in the channel via the remote phonon scattering mechanism [35] will still be limited as in SiO_2. This argument explains why HfO_2 can be integrated into a gate stack with high mobility and suggests that the formation of a compositionally graded interface with silicon [12,36] is crucial for both hafnia and zirconia dielectrics to preserve high electron mobility. On the other hand, only few metals can be incorporated into a silica matrix, even at low content, without inducing a reconstruction of its structure; this offers a rationale for the selection of candidate high-k oxides as well as of doping agents of HfO_2. We have shown that *ab initio*, extensive, and large-scale simulations are critical to elucidate the behavior of these complex materials, and open new avenues for the investigation of the physics of noncrystalline alloys.

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