Optical properties of monoclinic HfO$_2$ studied by first-principles local density approximation $+ U$ approach

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Hafnium dioxide (HfO$_2$) is widely studied both experimentally and theoretically due to its excellent dielectric properties, wide band gap, and high melting point, etc. [1,2]. It has been widely used in optical and protective coatings, capacitors, and phase shifting masks as one of the most promising high dielectric constant materials [3,4].

There are three polymorphs of HfO$_2$ existing at atmospheric pressure [3]: the monoclinic, the tetragonal and the cubic fluorite, denoted as m-, t-, and c-HfO$_2$, respectively. It has been known that the optical properties of thermally annealed samples depend on their preparation process and therefore the resulting structural details. In the thin films of m-HfO$_2$ grown on amorphous silica substrates, a small shoulder at the threshold of the absorption spectra has been detected [7]. Following experimental investigations have ruled out possible defect-related origins [8], and have noticed that the spectral weight of the shoulder increases with the crystallite size in the films [9]. On the other hand, no shoulder structure has been observed in both the tetragonal phase and cubic phase, can be understood as a consequence of the reconstruction of the electronic states near the band edge following the adjustment of the crystal structure. The existence of a similar shoulder-like-structure in the monoclinic phase of ZrO$_2$ is predicted.

In this paper, we use the LDA+$U$ scheme formulated by Loschen et al. [17] to investigate the electronic structures and optical properties of m-HfO$_2$. The on-site Coulomb interactions of 5$d$ orbitals on Hf atom ($U^d$) and of 2$p$ orbitals on O atom ($U^p$) are determined so as to reproduce the experimental value of band gap. We find that the imaginary part of the (average) dielectric function exhibits a shoulder structure at the edge of the band gap, the existence of which is actually robust against the perturbation with respect to $U$ values.

The band structures of m-HfO$_2$ have been calculated within the framework of local density approximation (LDA) and generalized gradient approximation (GGA), with further including spin-orbit interactions [10]. However, the resulting band gap is about 3.98 eV, much smaller than the experimental value, 5.7 eV [8]. The GW approximation, which can address the electron correlations to the some extent, gives the gap value as 5.78 eV, very close to the experimental one [11]. Nevertheless, the GW method demands considerable numerical resources. Another technique to include correlation effect with less computational efforts is the so-called LDA+$U$ or GGA+$U$ approach, where $U$ is the on-site Coulomb interaction [12]. Compared with LDA (GGA), the LDA (GGA) + $U$ approach can produce qualitative improvements, e.g., see Refs. [12,14]. A slightly extension of the approach, i.e., the LDA + $U^d$ + $U^p$ and GGA + $U^d$ + $U^p$, where the superscripts, $f$, $d$, and $p$, represent orbitals, has been employed in the studies of CeO$_2$ and c-HfO$_2$, respectively. And enhanced descriptions of the electronic structures have been obtained [13,16].

In our calculation, the density functional theory simulations are performed by using the LDA with CA-PZ functional and the LDA+$U$ approach as implemented in the CASTEP code (Cambridge Sequential Total Energy Package) [18]. For Hf and O atoms, the ionic cores are characterized by plane-wave ultrasoft pseudopotentials. The 5$d^2$ and 6$s^2$ electrons in Hf, 2$s^2$ and 2$p^4$ in O, are explicitly treated as valence electrons. The plane-wave cut off energy is 380 eV. The Brillouin-zone in-
tegration is performed over the 24 × 24 × 24 grid sizes using the Monkhorst-Pack method for structure optimization. This set of parameters assures the total energy convergence of 5.0 × 10^{-6} eV/atom, the maximum force of 0.01 eV/Å, the maximum stress of 0.02 GPa and the maximum displacement of 5.0 × 10^{-4} Å. After optimizing the geometry structure, we calculate the electronic structures and optical properties of HfO2. More numerical details can be found elsewhere [10].

The space group of m-HfO2 is P21/c and the local symmetry is C2h-5. The experimental values of the lattice constants a, b, c, and the angle β are following: a = 0.5117 nm, b = 0.5175 nm, c = 0.5291 nm, and β = 99.2° [19]. The LDA calculation of the perfect bulk m-HfO2 is performed to determine the optimized parameters in order to check the applicability and accuracy of the ultrasoft pseudopotential. The results, a = 0.5225 nm, b = 0.5349 nm, c = 0.5365 nm, and β = 99.5° [19] and other theoretical values [20, 22]. However, the value of the band gap $E_g$ is around 3.24 eV, much smaller than the experimental value (∼ 5.7 eV). This is due to the fact that the density functional theory usually undervalues the energy of 5d orbitals of Hf atom, lowering the bottom level of conduction bands.

In order to reproduce the band gap, we first introduce $U^d$ for 5d orbitals of Hf atom. Using the experimental lattice parameters as initial values, we optimize geometry structure and calculate the band structure and density of state (DOS) of m-HfO2. The band gap $E_g$ obtained from the band structure is shown in Fig. 1(a) as a function of $U^d$. It can be seen that $E_g$ firstly increases, and then drops with the increase of $U^d$, showing a maximum value (∼ 4.02 eV) at $U^d = 8.0$ eV, where the lattice parameters of the optimized structure are a = 0.5382 nm, b = 0.5370 nm, c = 0.5474 nm, and β = 99.7°. The maximum $E_g$ value is still smaller than the experimental one. The saturation of $E_g$ with $U^d$ may be related to the approach of 5d states toward 6s and 5p states, though microscopic mechanism is not yet fully understood. Next, we introduce $U^p$ for 2p orbital of O atom, while keeping $U^d$ fixed at 8.0 eV. Different from Fig. 1(a), the results in Fig. 1(b) shows a monotonic increase in $E_g$ as a function of $U^p$. When $U^d = 8.0$ eV and $U^p = 6.0$ eV, the calculated band gap of m-HfO2 is 5.70 eV, well coinciding with the experiment. The lattice parameters of the optimized structure are a = 0.5386 nm, b = 0.5331 nm, c = 0.5492 nm, and β = 99.6°.

By adopting the optimal U values as $U^d = 8.0$ eV, $U^p = 6.0$ eV, we perform the LDA+U calculation. The band dispersion is presented in Fig. 2(a). The bottom of the conduction band is located at the G point. Since the bottom is lifted to higher energy by introducing $U^d$, accompanied with the reconstruction of the conduction band, the DOS around 4.5 eV and 6.9 eV, which is separated in LDA without $U$ (not shown), has merged into one sharp structure at 6.8 eV (Fig. 2(b)) [16]. According to the partial DOS of Hf and O atoms in Figs. 2(c) and 2(d), we can see that just above and below the gap, the conduction band is predominantly constructed by Hf 5d states, while the valence band by O 2p states. Therefore, the low-lying optical excitations across the gap is mainly composed by the interband transitions from the O 2p to the Hf 5d orbitals.

Figure 3(a) shows the dielectric function of m-HfO2, with comparison to those of t-HfO and c-HfO. The real part, $\varepsilon_1$, exhibits a maximum at 6.57 eV. The calculated static dielectric constant is 3.32, coinciding with the experimental value [3, 23]. The imaginary part, $\varepsilon_2$, shows a maximum at 9.0 eV. The maximum, around 6.2, is very close to the experimental observation 6.0 [8], while the value obtained by LDA without U is around 8.7. Other optical properties, like optical conductivity, can be computed from the complex dielectric function [19]. We also.

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**FIG. 1.** (Color online) The band gap $E_g$ as a function of (a) $U^d$ and (b) $U^p$.**

**FIG. 2.** (Color online) The band structure and density of states (DOS) of m-HfO2 obtained by LDA+$U^d$+$U^p$ ($U^d = 8.0$ eV, $U^p = 6.0$ eV). (a) Band structure. The total DOS, the partial DOS of Hf and O atoms are shown in (b), (c) and (d), respectively.
FIG. 3. (Color online) Comparison of (a) dielectric functions and (b) total DOS of m-HfO₂ with t-HfO₂ and c-HfO₂ obtained by LDA+U^{d+c}. Inset in (a): Zoom-in view of the imaginary part of the dielectric function, \( \epsilon_2 \), near the gap edge.

Obtain the refractive coefficient \( n = 1.82 \), close to the experimental value 1.93 [3].

The calculated \( \epsilon_2 \) of t-HfO₂ and c-HfO₂ are presented in Fig. 3(a) for comparison. The values of \( U^d \) and \( U^p \) are determined so as to reproduce the experimental gap values. Here, the resulting \( U^d=8.25 \, \text{eV} \) (8.25 eV) and \( U^p=6.3 \, \text{eV} \) (6.25 eV) for t-HfO₂ (c-HfO₂ [16]). We find that \( \epsilon_2 \) exhibits similar spectral distributions between t-HfO₂ and c-HfO₂, with only a small shift along the energy direction (~ 1 eV). By contrast, the global spectral distribution of \( \epsilon_2 \) in m-HfO₂ is quite different from them. More interestingly, as shown in the inset of Fig. 3(a), a small shoulder structure emerges at the edge of the band gap (~ 6.0 eV) in m-HfO₂, which, on the other hand, cannot be found either in t-HfO₂ or in c-HfO₂. The exclusive presence of the shoulder structure is consistent with experimental observations [17].

In order to understand the origin of the shoulder, we compare the total DOS of the valence and conduction bands in m-HfO₂ with those in the other two phases. As shown in Fig. 3(b), the DOS in t-HfO₂ and c-HfO₂ are similar to each other, while there is a significant difference in m-HfO₂. In particular, at the edge of the valence band, the DOS in m-HfO₂ smoothly increases but there is a step feature in t-HfO₂ and c-HfO₂ at the edge. Furthermore, the conduction band in m-HfO₂ reveals a broad feature of DOS around 6.5 eV in contrast to t-HfO₂ and c-HfO₂, in which a peak appears near 6.0 eV. Since \( \epsilon_2 \) is given by the excitation from the valence band to the conduction band across the band gap, the difference of DOS between m-HfO₂ and t-(c-)HfO₂ is indicative of the presence of the shoulder in \( \epsilon_2 \) only for m-HfO₂. A more detailed microscopic origin of the shoulder, such as the assignment of the momentum and band index dominating the absorption at the shoulder, remains to be resolved in the future. We note that the shoulder structure also appears at the edge of the band gap in the standard LDA calculation without \( U \) (not shown). This means that the reconstruction of the electronic states due to the monoclinic structure is crucial for the shoulder structure, as indicated by the previous experimental investigations [7].

The experimental studies for HfO₂ have shown that thermally annealed films [8], crystallite films [13], and thin films grown on amorphous silica substrates [7] reveal a shoulder-like feature in \( \epsilon_2 \). The experimental data showing the annealing effect taken from Ref. 8 are plotted together with the present theoretical result in Fig. 4. We find that the calculated small shoulder appears at almost the same energy (~ 6.0 eV) as experimental shoulder for the annealed samples. This means that the present LDA+U^{d+c} approach can reproduce an essential feature of the electronic structures in crystalline m-HfO₂. We note that the magnitude of \( \epsilon_2 \) is different from the experimental ones. The difference may partly come from the fact that the samples of m-HfO₂ reported in Ref. 8 mix with small amount of orthorhombic and tetragonal HfO₂.

Finally, it is worth to mention that we have additionally carried out the calculation on ZrO₂, using the same strategy. In many aspects, ZrO₂ resembles its twin oxide, HfO₂, though the electron correlations are generally believed to be weaker. The shoulder-like feature in the dielectric function is also found in the monoclinic phase of ZrO₂, while absent in the other two phases (tetragonal and cubic), similar to other theoretical results obtained.
from full-relativistic calculation \cite{24}. This seems not consistent with experiments, since no shoulder-like structure has been reported \cite{24,26}. Here we would like to point out that in order to prepare pristine crystallized ZrO\textsubscript{2} with monoclinic structure, the temperature of thermal annealing should reach over 1,000 °C \cite{27}, which means that up to now, for the ZrO\textsubscript{2} samples used in the optical measurements, the monoclinic component may not be dominant. Based on our results, we predict the emergence of the shoulder-like structure in the imaginary part of the dielectric function with the monoclinic ZrO\textsubscript{2} (m-ZrO\textsubscript{2}) being prevalent in the mixture of the three phases.

In summary, the on-site Coulomb interactions for the 5\textit{d} orbital of Hf atom (\textit{U\textsubscript{d}}) and the 2\textit{p} orbital of O atom (\textit{U\textsubscript{p}}) are introduced into the first-principles LDA band calculation of m-HfO\textsubscript{2}. With the optimal values of \textit{U\textsubscript{d}} = 8.0 eV, \textit{U\textsubscript{p}} = 6.0 eV, the experimental band gap is reproduced. A shoulder-like structure at the edge of the band gap in the imaginary part of the dielectric function is obtained, which is consistent with the experiments. The presence of the shoulder in m-HfO\textsubscript{2} and its absence in t-HfO\textsubscript{2} and c-HfO\textsubscript{2} indicate the impact of the crystal structure on the electronic bands and optical properties. The existence of a similar shoulder-like structure in m-ZrO\textsubscript{2} is predicted.

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