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Computational investigation of the phase stability and the electronic properties for Gd-doped HfO$_2$

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Rare earth doping is an important approach to improve the desired properties of high-k gate dielectric oxides. We have carried out a comprehensive theoretical investigation on the phase stability, band gap, formation of oxygen vacancies, and dielectric properties for the Gd-doped HfO$_2$. Our calculated results indicate that the tetragonal phase is more stable than the monoclinic phase when the Gd doping concentration is greater than 15.5%, which is in a good agreement with the experimental observations. The dopant's geometric effect is mainly responsible for the phase stability. The Gd doping enlarges the band gap of the material. The dielectric constant for the Gd-doped HfO$_2$ is in the range of 20–30 that is suitable for high-k dielectric applications. The neutral oxygen vacancy formation energy is 3.2 eV lower in the doped material than in pure HfO$_2$. We explain the experimental observation on the decrease of photoluminescence intensities in the Gd-doped HfO$_2$ according to forming the dopant-oxygen vacancy complexes. © 2014 AIP Publishing LLC.
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Hafnia has attracted considerable attention because of its potential applications as the high—k gate dielectric oxide in ultrascaled complementary-metal-oxide-semiconductor (CMOS) devices. It has a wide band gap and is thermally stable on the Si substrate. Hafnia also has a much higher dielectric constant compared to SiO$_2$. These desirable properties make hafnia a good replacement of SiO$_2$ as the gate dielectric material in downscaling devices. Actually, hufnium-based oxides have been successfully introduced into the 45-nm technology node.[1]

HfO$_2$ has three polymorphs. At ambient condition, it has a monoclinic (m) phase and undergoes a transition to the tetragonal (t) phase at 2000 K and to the cubic (c) phase at 2900 K. The higher symmetry tetragonal phase is desired for device applications because it has a larger band gap[2] and a higher permittivity[3–5] compared to the lower symmetry monoclinic phase. There exist considerable experimental and theoretical studies[4–11] on the stabilization of the tetragonal phase HfO$_2$ by various doping elements. Rare earth (RE) doped HfO$_2$ is especially interesting because the doping does not produce gap states.[8] The RE stabilized t-HfO$_2$ reduces leakage current by three orders of magnitude compared to pure m-HfO$_2$.[4] The RE doping also enlarges the band gap, increases the permittivity, and suppresses the formation of oxygen vacancies.[12] Recent experimental studies[4,6] found when the Gd doping is beyond a certain concentration around 15%–20% the doped HfO$_2$ is completely transformed to the tetragonal phase. The density functional theory (DFT) calculations were also used to investigate the phase stability, point defects and defect complexes in Gd-doped HfO$_2$.[8,13,14] These calculations were done for a fixed doping concentration, and could not accurately predict at which doping concentration the phase transition occurs. The authors in Ref. 8 also claimed that the dopants with ionic radii smaller than Hf tend to stabilize the tetragonal phase and larger dopants favour the cubic phase. However, they did not explain why

Ge is a very effective stabilizer of the tetragonal phase while Ti supports the tetragonal phase very weakly although two elements have a very similar ionic radius.[8,9] Ce which has an ionic radius larger than Hf appears to be a better stabilizer of the tetragonal phase than C, Ti, and Sn.[9] Based on the density-functional calculations, Liu *et al*. discussed the effect of Gd doping on the band gap at the fixed concentration of 6.25%.[13] Interestingly, the authors found that there exist four sevenfold coordinated Hf atoms in the cubic phase they calculated.[13] It is obvious our understanding on the mechanism of phase stability and the effect of RE doping in HfO$_2$ is far from complete. Furthermore, the calculations also showed that the formation energy of an oxygen vacancy is smaller in the Gd-doped case than in pure HfO$_2$.[14] These calculations seem to conflict with the experimental observation[12] that the Gd doping suppresses the formation of oxygen vacancies.

In this Letter, employing the state-of-the-art density-functional theory calculations, we present a comprehensive study of Gd doping in HfO$_2$. We investigate the effect of Gd doping on the phase stability and find that beyond the doping concentration of 15.5% the tetragonal phase is more stable than the monoclinic phase. Since we have not included any effects from the surfaces, interfaces and oxygen vacancies in our calculations, the stability of the tetragonal phase is interpreted by the geometric effect of the dopant atoms. We also investigate the dependence of the band gap and the dielectric properties on the Gd concentrations. We further explain the experimental observations on decreasing of photoluminescence (PL) intensities according to forming the dopant-oxygen vacancy complexes.

The calculations are performed within the framework of DFT as implemented in Vienna *Ab-initio* Simulation Package (VASP) codes[15,16] with the generalized gradient approximation (GGA) for the exchange-correlation potential.[17] We use the PAW (projector augmented wave) pseudopotentials[18,19] to describe interactions between ions and

TABLE I. The optimized structural parameters for the monoclinic, tetragonal, and cubic HfO$_2$. Only nontrivial parameters are presented.

Phase	This work	Other theory[a]	Experiment[b]
Monoclinic	$a = 5.15$ Å	$a = 5.12$ Å	$a = 5.12$ Å
	$b = 5.21$ Å	$b = 5.20$ Å	$b = 5.17$ Å
	$c = 5.31$ Å	$c = 5.28$ Å	$c = 5.30$ Å
	$\beta = 99.69°$	$\beta = 99.7°$	$\beta = 99.2°$
Tetragonal	$a = 5.08$ Å	$a = 5.06$ Å	$a = 5.15$ Å
	$c = 5.23$ Å	$c = 5.20$ Å	$c = 5.29$ Å
Cubic	$a = 5.08$ Å	$a = 5.05$ Å	$a = 5.08$ Å

[a]Reference 8.
[b]Reference 22–24.

valence electrons. The valence electron configurations are $5p^65d^36s^1$ for Hf, $2s^2sp^4$ for O, and $5p^65d^16s^2$ for Gd. The supercells containing 96 atomic sites are employed for simulating all bulk phases. For various doping concentrations [defined as $N_{Gd}/(N_{Gd} + N_{Hf}) \times 100\%$, N_{Gd} and N_{Hf} are the numbers of Gd and Hf atoms in the supercell, respectively], the Gd atoms randomly occupy the Hf sites determined by the SQS (special quasirandom structure) method.[20] The energy cutoff of 550 eV is used for the plane basis and a $2 \times 2 \times 2$ Monkhorst-Pack grid for the Brillouin zone sampling. The atomic positions and cell parameters are allowed to relax in the calculations. These parameters result in a good convergence and are also used in several previous calculations.[8,11,21] The optimized structural parameters are presented in Table I, and our results are in good agreement with the previous calculated and experimental values. The dielectric properties are calculated using the density functional perturbation theory.[25] Since it is well known that the GGA exchange-correlation potential underestimates the band gap, we employ the hybrid functional to obtain the correct band gap. For the monoclinic phase, we obtain a band gap of 5.65 eV compared to the experimental value[5] of 5.7 eV, a great improvement over the GGA value of 4.03 eV. So we will present the results of the band gap and the density of states calculated with the hybrid functional.

The total energies of the monoclinic, tetragonal, and cubic phases are calculated for the Gd doping concentration range from 0 up to 25%. Although the cubic phase is more stable than the monoclinic phase when the doping concentration is greater than ∼20%, it is unstable with respect to the tetragonal phase for the Gd concentration range we consider. The total energies for the monoclinic and tetragonal phases and the energy difference between the two phases are presented in Fig. 1(a). The energy difference between the monoclinic and tetragonal phases without doping is 0.16 eV per HfO$_2$, which is in agreement with the previous DFT-GGA calculated value of 0.17 eV.[8] Our calculated results indicate that the tetragonal phase becomes more stable than the monoclinic phase when the Gd doping concentration is greater than 15.5%. This Gd doping concentration is consistent with the experimental observations.[4,6] The Gd doping concentration we predict at which the phase transition occurs is close to the value of 13% estimated based on the structural energy difference at the Gd concentration of 3.125% (i.e., one doping Gd atom in the 96-atom supercell).[8] The authors[8] also predicted that the cubic phase is more stable than the tetragonal phase when the Gd doping concentration greater than 6.7%. This rules out the stability of the tetragonal phase which is inconsistent with the experimental observation that the tetragonal phase is stabilized in Gd-doped HfO$_2$.[4] Furthermore, since in our calculations we have not included any contributions from surfaces, interfaces, and oxygen vacancies, the phase transition from the monoclinic phase to the tetragonal phase is completely caused by the dopant effects, i.e., the electronic and geometric effects.[26] From Fig. 1(b), we see that the volume difference between the two phases follows the same trend of the total energy difference. We can rationalize this correlation by the elastic energy release. A detailed check of the optimized atomic structures in the heavily doped tetragonal phases (for example, the doping concentration >18%) shows that most Hf atoms have seven nearest neighbours. So for these heavily doped cases Hf atoms in the supercell prefer to have a sevenfold coordinated monoclinic-phase-like environment. Previous study also found that there exist sevenfold coordinated Hf atoms in the Gd-doped cubic phase.[13] Because the undoped m-HfO$_2$ has a substantially larger volume than that of the undoped t-HfO$_2$, this explains why the volume expansion favours the tetragonal phase. On the other hand, the Gd doping in m-HfO$_2$ increases the volume and the elastic energy (due to volume expansion)
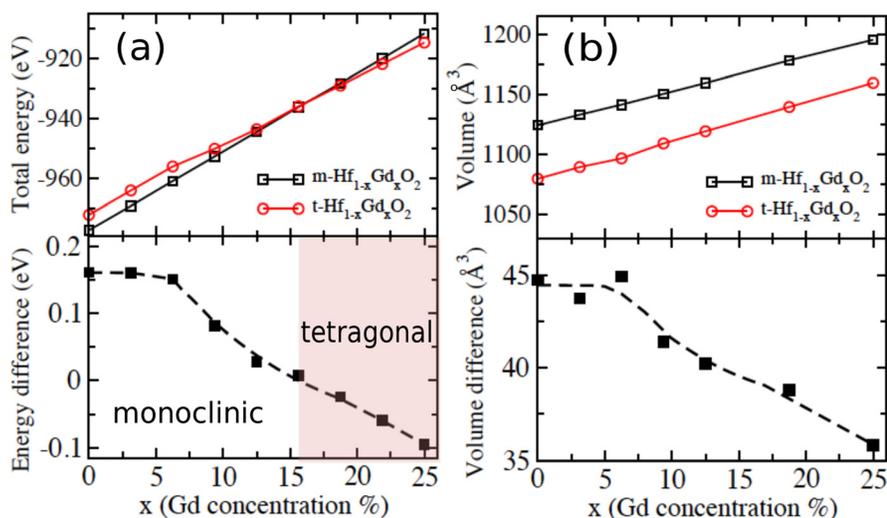

FIG. 1. Total energies and energy difference (a) and volume and volume difference (b) for the monoclinic and tetragonal phases as a function of the Gd concentration. The dashed lines are given for guiding the eyes. The shaded part indicates that the tetragonal phase is more stable than the monoclinic phase.

and makes the monoclinic phase less favourable. Therefore, the doping effects include both the volume expansion and the change of the local atomic environment.

The calculated bang-gap for the monoclinic and tetragonal phases is presented in Fig. 2. For the undoped HfO_2, the band gap of the tetragonal phase is 0.7 eV larger than that of the monoclinic phase. The band gap almost linearly increases for the monoclinic phase with increasing the Gd concentration, while for the tetragonal phase, it linearly decreases with increasing the Gd concentration. The reduction of the band gap size in the Gd-doped t-HfO_2 may be related to the fact that some Hf atoms in the doped case have a monoclinic-phase-like local atomic configuration. We predict a band gap of 5.97 eV at the 25% Gd concentration for the monoclinic phase. This is an increase of 0.32 eV in the band gap size compared to pure m-HfO_2. The band gap size is in coincident to the experimental value of 5.97 eV at the 25% Gd concentration for the amorphous phase.[12] The band gap increase is somehow larger than the experimental value of 0.16 eV for the amorphous phase.[12] Figure 3 shows the density of states for the monoclinic phase at the Gd concentrations of 0%, 12.5%, and 25%. We see there is no gap state by the Gd doping. The p and d bands for the Gd doping cases become narrower compared to those for the undoped case. This can be explained by the volume expansion (see Fig. 1(b)) by the Gd doping. The s, p, and d bands move towards the higher energy direction, especially the shift-up of the d bands leads to enlarge the band gap. We find that the Gd-p states are located at the energy range close to the O-s states and the interaction between the Gd-p and O-s states shifts the O-p and (Hf,Gd)-d bands up.

We calculate the static dielectric constants at various Gd concentrations. For the undoped case, we obtain an average dielectric constant of 18.9 and 75.0 for the monoclinic phase and the tetragonal phase, respectively. Our result for the monoclinic phase is in good agreement with a previous GGA calculation of 18[3] and the experimental measurements of 16–20.[5] For the Gd-doped cases, the dielectric constant increases with increasing the Gd concentration for the monoclinic phase. At the Gd concentration of 12.5% that the monoclinic phase is still maintained, the calculated dielectric constant is 25.5. For the tetragonal phase, the dielectric constant dramatically decreases up on the Gd doping. At the Gd concentration of 12.5%, it is 27 and becomes 24 at the Gd
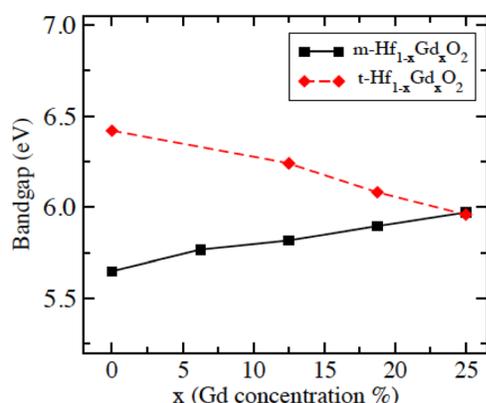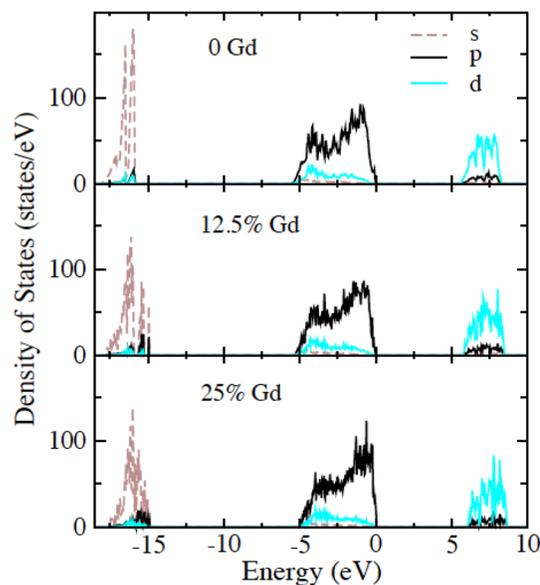

FIG. 3. Density of states for the monoclinic phase at the Gd concentrations of 0%, 12.5%, and 25%.

concentration of 25%. Therefore, the Gd-doped HfO_2 with the dielectric constant in the range of 20–30 is promising for high-k dielectric applications.

Previous experimental studies[12] found that the Gd doping could suppress the formation of oxygen vacancies. In order to understand this we calculate the oxygen vacancy formation energies in the doped and undoped cases. As it is well known that the formation energy of a defect depends on the chemical potentials, as well as on the charge state if it is charged.[27,28] The formation energy of an oxygen vacancy is defined as follows:

$$E_f = E_{Hf_{32-N}Gd_NO_{63}} - E_{Hf_{32-N}Gd_NO_{64}} + \mu_O + q(\varepsilon_F + E_{VBM}),$$
(1)

where $E_{Hf_{32-N}Gd_NO_{63}}$ and $E_{Hf_{32-N}Gd_NO_{64}}$ are the total energy of the system with or without an oxygen vacancy, N = 0 or 1. For N = 0, the system is undoped by Gd and N = 1 means there is one hafnium atom replaced by a Gd atom. μ_O is the oxygen chemical potential. q is the charge state, and ε_F and E_{VBM} are the Fermi energy and the valence band maximum, respectively. For the Gd-doped case, we consider an oxygen vacancy which is located next to the Gd dopant. An Oxygen atom in the monoclinic phase has either three or four nearest neighbours, and the oxygen vacancy formation energy for the charge neutral state is 0.14 eV lower at the fourfold coordinated site than at the threefold coordinated site. We calculate the formation energies at the fourfold coordinated site for the neutral and charged states and the results are given in Table II. We see that it is easier to form oxygen vacancies for the doped case relative to the undoped case. For the neutral oxygen vacancy, we obtain the formation energies of 6.50 eV (undoped) and 3.27 eV (doped) under oxygen rich conditions. A previous study[14] found that the oxygen vacancy formation energy decreases from 5.88 eV (undoped) to 3.35 eV (doped), which is in agreement with our results. But our formation energy of 6.50 eV for the undoped case is in better agreement with other calculated values[21,29] of 6.73 eV

FIG. 2. Bandgap for the monoclinic and tetragonal phases as a function of the Gd concentration.

TABLE II. Oxygen vacancy formation energies for the undoped and doped HfO$_2$. All units are in eV.

	E$_f$ (doped)	E$_f$ (undoped)	E$_f$ (doped)-E$_f$ (undoped)
V$_O^0$	$8.18 + \mu_O$	$11.41 + \mu_O$	-3.23
V$_O^+$	$2.14 + \mu_O + (\varepsilon_F + E_{VBM})$	$5.59 + \mu_O + (\varepsilon_F + E_{VBM})$	-3.45
V$_O^{2+}$	$-0.80 + \mu_O + 2(\varepsilon_F + E_{VBM})$	$-0.61 + \mu_O + 2(\varepsilon_F + E_{VBM})$	-0.19

and 6.63 eV. An oxygen vacancy in HfO$_2$ plays a role as a donor and Gd$_{Hf}$ as an acceptor. Two defects attract each other and thus lows the formation energy of an oxygen vacancy in the doped HfO$_2$. In Table II, it also shows that the formation of V$_O^{2+}$ near a Gd dopant is only slightly favourable compared to the formation of V$_O^{2+}$ in the undoped HfO$_2$. In a previous experimental study,[12] the authors observed a decrease of the PL intensity in the Gd-doped HfO$_2$ compared to the undoped HfO$_2$. We argue that the decrease of PL intensities is because the dopants and the oxygen vacancies attract each other and form the dopant-oxygen vacancy complexes, thus removes the oxygen vacancy states from the band gap.[13,30,31] In Ref. 13, the authors had investigated the (Gd$_{Hf}$)$_2$V$_O$ complex in HfO$_2$ and found that there is no gap state for the complex. Nadimi *et al.*[31] calculated the formation energies and the energy levels of all possible (La$_{Hf}$)$_2$V$_O$ atomic configurations. The average energy level measured from the valence band maximum was calculated to be 3.63 eV for T = 20 °C and 3.62 eV for T = 120 °C, which has a large up-shift compared to the energy level of 1.87 eV for V$_{O4}$ and 2.33 eV for V$_{O3}$. The average energy level is eventually out of the band gap of perfect HfO$_2$. We have also studied the nine possible atomic configurations of (Gd$_{Hf}$)$_2$V$_O$ (three different atomic configurations for (Gd$_{Hf}$)$_2$V$_{O3}$ and six atomic configurations for (Gd$_{Hf}$)$_2$V$_{O4}$), and found that the energy level corresponding to the lowest energy atomic configuration moves up close to the conduction band.[30]

In summary, we have performed the density functional calculations for the Gd-doped HfO$_2$. The tetragonal phase is found to be more stable than the monoclinic phase when the Gd doping concentration is greater than 15.5%, and the cubic phase is never stable for the Gd concentration range we consider. For the Gd-doped HfO$_2$, the band gap linearly increases (decreases) with increasing the Gd concentration in the monoclinic (tetragonal) phase. But overall the band gap for the Gd-doped HfO$_2$ is larger than that of the pure monoclinic HfO$_2$. The dielectric constants are enhanced by the Gd doping. The experimental observation on the decrease of PL intensities for the Gd-doped HfO$_2$ is explained according to forming the dopant-oxygen vacancy complexes.

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