

Oxygen pressure dependence of HfO₂ stoichiometry: An *ab initio* investigation

C. Tang and R. Ramprasad^{a)}

Department of Chemical, Materials and Biomolecular Engineering, Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269

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The oxygen pressure dependence of the formation of excess O vacancies and interstitials in monoclinic HfO₂ was investigated by performing first principles and thermodynamic calculations. Upper and lower critical oxygen pressures are identified that heavily favor the formation of oxygen interstitials and vacancies, respectively. The ratio of these critical pressures can be specified unambiguously as the sum of the formation energies of O vacancies and interstitials at 0 K obtained from *ab initio* calculations. © 2007 American Institute of Physics. [DOI: 10.1063/1.2756107]

The desire for continued miniaturization of microelectronic devices has spurred considerable research on high dielectric constant (or high- κ) materials such as HfO₂ and ZrO₂ as prospective substitutes for conventional SiO₂ gate dielectrics. Due to their high thermodynamic stability in contact with Si,¹⁻³ these materials are expected to be resistant to the formation of interfacial silica and silicide, which are both detrimental to device performance. However, contradictory to the above expectations, the formation of silica, Hf (or Zr) silicide, and silicate at the interfaces has been observed.⁴⁻⁹ Cho *et al.*⁴ found that the formation of Hf silicide is intimately related to the deficiency of oxygen, and Qiu *et al.*⁸ reported the transition of Hf silicide into Hf silicate during postannealing in an oxygen ambient. It has been proposed that these interfacial reactions could be closely related to high diffusivity of oxygen and due to nonstoichiometric metal oxide phases.¹⁰ Our recent first principles calculations on Si:HfO₂ heterostructures^{11,12} imply that there exist thermodynamic and kinetic driving forces for the segregation of oxygen vacancies and interstitials from nonstoichiometric HfO₂ to the interface, favoring the formation of interfacial silicide and silica.

An issue that naturally follows is how we can control the concentration of oxygen defects or the stoichiometry of HfO₂. An understanding of the relationship between the stoichiometry and external factors such as temperature and oxygen pressure would be valuable. However, available sparse experimental data cover only a small stoichiometry range of HfO₂.¹³ In the current work, we explore the oxygen pressure and temperature dependence of the concentration of oxygen defects in bulk HfO₂ via *ab initio* calculations. Similar *ab initio* calculations have been performed recently to study the effects of O vacancies on CeO₂ stoichiometry.¹⁴

Density functional theory (DFT) calculations of the formation energies of an O defect (vacancy or interstitial) in HfO₂ were performed using the VASP code¹⁵ with the Vanderbilt ultrasoft pseudopotentials,¹⁶ the generalized gradient approximation (GGA) utilizing the PW91 functional,¹⁷ and a cutoff energy of 400 eV for the plane wave expansion of the wave functions. Various defect concentrations were considered by creating one O defect in a bulk HfO₂ supercell of various sizes. A Monkhorst-Pack *k*-point mesh of 4 × 4 × 4

was used for the smallest 1 × 1 × 1 supercell that contained four Hf and eight O sites, and the *k*-point mesh was proportionately decreased for larger supercells.

The formation energy of an O vacancy (E_v^f) or interstitial (E_i^f) can be defined as

$$E_v^f = E_{\text{vac}} - E_{\text{perf}} + \mu_{\text{O}_2}/2, \quad (1)$$

$$E_i^f = E_{\text{int}} - E_{\text{perf}} - \mu_{\text{O}_2}/2, \quad (2)$$

where E_{vac} , E_{int} , and E_{perf} represent the energies of the system with an O vacancy, an O interstitial, and the perfect system, respectively, and μ_{O_2} is the chemical potential of a gaseous O₂ molecule. μ_{O_2} can be further defined as

$$\mu_{\text{O}_2} = \mu_{\text{O}_2}^0 + kT \ln(P_{\text{O}_2}/P_{\text{O}_2}^0) = \mu_{\text{O}_2}^0 + kT \ln(p_{\text{O}_2}), \quad (3)$$

where $\mu_{\text{O}_2}^0$ is the energy of an O₂ molecule calculated at 0 K corresponding to a pressure of $P_{\text{O}_2}^0$, P_{O_2} is the oxygen pressure in the system, k is the Planck constant, and T is the temperature. Similar treatments in terms of chemical potentials can be found elsewhere.^{14,18,19} Since $P_{\text{O}_2}^0$ is unknown, but $P_{\text{O}_2}/P_{\text{O}_2}^0 (=p_{\text{O}_2})$ is well defined, all references to oxygen pressure in this letter deal with p_{O_2} .

The temperature and oxygen pressure dependence of O defect formation energies can be illustrated using a 2 × 2 × 2 monoclinic HfO₂ supercell which accommodates 32 Hf and 64 O atomic sites. In this supercell, we created an O vacancy at a fourfold site or an O interstitial near a threefold site since these sites have low defect formation energies.²⁰ E_v^f was calculated using VASP to be 6.5 eV at 0 K. At 0 K, E_v^f is independent of oxygen pressure, as reflected by the horizontal dashed line in Fig. 1(a). At $T > 0$ K, the influences of the entropy are not considered in Eqs. (1) and (2) since the temperature of HfO₂ film processing (such as annealing) is relatively low compared with its melting point. Under this assumption, E_v^f linearly decreases with decreasing $\ln(p_{\text{O}_2})$ at $T > 0$ K and reaches zero at a critical p_{O_2} . For pressures lower than the critical p_{O_2} , the stoichiometric HfO₂ structure is unstable and O vacancies are spontaneously created. When T is lowered, this critical p_{O_2} required to create a single O vacancy in the supercell is also lowered.

For O interstitials, E_i^f was determined as 1.7 eV at 0 K, as shown in Fig. 1(b). In contrast to the vacancy case, E_i^f for

^{a)}Electronic mail: rampi@ims.uconn.edu

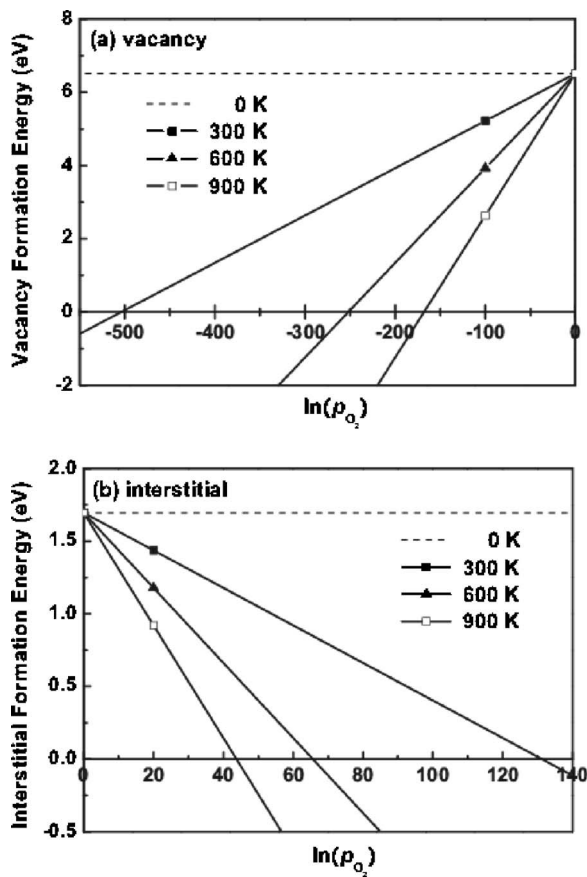


FIG. 1. Dependence of the calculated formation energy of an O vacancy (a) and an O interstitial (b) in a $2 \times 2 \times 2$ HfO_2 supercell on oxygen pressure and temperature.

the O interstitial linearly decreases for increasing $\ln(p_{\text{O}_2})$ at $T > 0$ K. As T is increased, the critical p_{O_2} for O interstitial formation is reduced. The critical pressures, $p_{\text{O}_2}^c$, for both vacancy and interstitial cases can be obtained from Eqs. (1) and (2) by setting E_v^f and E_i^f to zero, respectively.

Using supercells of various sizes, we calculated the defect formation energies at 0 K for different defect concentrations (corresponding to different stoichiometries or x values of HfO_x), as shown in Table I. For each case, the values of $p_{\text{O}_2}^c$ (for both vacancy and interstitial) at various T were determined using the above method. Thus a mapping between HfO_x stoichiometries and $p_{\text{O}_2}^c$ values can be established at different T , as illustrated in Fig. 2. The currently available experimental data, also shown in Fig. 2, only cover the narrow stoichiometry range of $1.9999 < x < 2.0001$.¹³ In Fig. 2, the P_{O_2} axis on the right-hand side along with the experimen-

TABLE I. HfO_x stoichiometry dependence of defect formation energies (eV) at 0 K.

Supercell size	Vacancy		Interstitial	
	x	E_v^f	x	E_i^f
$4 \times 2 \times 2$	1.984	5.26	2.016	0.46
$2 \times 2 \times 2$	1.969	6.51	2.031	1.69
$2 \times 2 \times 1$	1.938	6.34	2.063	1.50
$2 \times 1 \times 1$	1.875	6.53	2.125	1.77
$1 \times 1 \times 1$	1.750	6.53	2.250	1.79

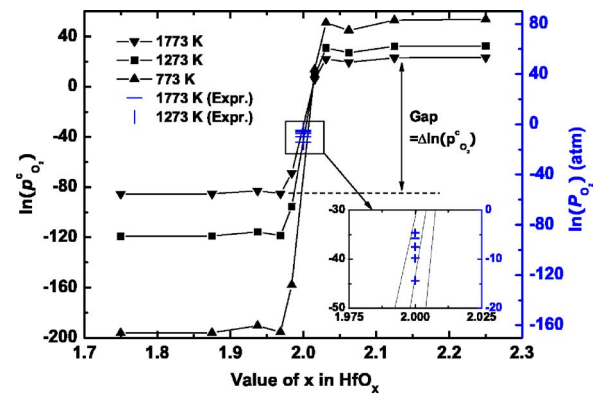


FIG. 2. (Color online) Calculated (left axis) and experimental (right axis) relationships between the stoichiometry of HfO_x , temperature, and critical oxygen pressure. The inset shows the details of matching between the calculated and experimental data.

tal data were shifted vertically with respect to the left-hand side p_{O_2} (arbitrary) axis such that the experimental data match the calculation results. This shifting of the axis allows for a mapping of p_{O_2} to P_{O_2} and is justified by the fact that according to Eq. (3), the difference in the values of $\ln(p_{\text{O}_2})$ and $\ln(P_{\text{O}_2})$ is a constant.

Recently Baik *et al.*⁵ have observed an increase in HfO_2 film thickness of about 3% during annealing and have suggested the incorporation of oxygen from the ambient atmosphere into HfO_2 as a possible reason for the thickness increase. We investigated the influence of O interstitials on HfO_x volume by relaxing the lattice vectors of supercells and found that one O interstitial could increase the supercell volume by 0.2% for a $2 \times 2 \times 2$ supercell and by 2.88% for a $1 \times 1 \times 1$ supercell. Although the mechanism of HfO_2 volume change could be complicated by many factors, the conclusions by Baik *et al.*⁵ qualitatively agree with our simulation results.

It can be seen from Fig. 2 that the pressure-stoichiometry profile can be divided into three parts with respect to the stoichiometry parameter x . When $x < 1.97$ the critical pressures are very low and the curves are nearly flat, converging to a lower critical pressure; in the range $1.97 < x < 2.03$ the pressures rise sharply; when $x > 2.03$ the pressures are high and the curves become flat again, converging to an upper critical pressure. As the temperature increases, the pressure gap between the upper and lower critical pressures decreases.

A larger pressure gap implies the possibility of better control of stoichiometry. Although p_{O_2} has arbitrary units, the pressure gap as defined in Fig. 2 [$\Delta \ln(p_{\text{O}_2}^c)$] can be determined uniquely by combining Eqs. (1) and (2) and setting E_v^f and E_i^f to zero (as this will correspond to the critical pressures), resulting in

$$E_{\text{vac}} + E_{\text{int}} - 2E_{\text{perf}} = kT\Delta \ln(p_{\text{O}_2}^c). \quad (4)$$

In Eq. (4), the left side is the energy needed to remove an O atom from a perfect lattice and to insert it into another perfect lattice, which can be unambiguously determined using *ab initio* calculations.

In Eqs. (1) and (2) the entropy term $-T\Delta S$ was ignored, which may decrease the defect formation energy by a few kT 's and affect the shape of the curves in Fig. 2 at high temperatures. Nevertheless Fig. 2 gives information on controlling O defect formation during film deposition and an-

nealing. As the temperature increases, more O defects are likely to occur, as indicated by the decrease in the pressure gap and the increase (decrease) of oxygen pressure required for the formation of an O vacancy (interstitial). During annealing, these excess defects could diffuse to the Si:HfO₂ interface and contribute to the formation of interfacial silicide or silica phases. Figure 2 implies that the type of excess O defect (and therefore the nature of the interfacial phase) can be adjusted by tuning the oxygen pressure. This has been attempted experimentally by Qiu *et al.*,⁸ who converted the interfacial Hf silicide into Hf silicate by increasing the oxygen content of the annealing atmosphere.

In summary, we have illustrated the dependence of oxygen defect formation in HfO₂ on temperature and oxygen pressure. These results could help control the stoichiometry of HfO₂ and the formation of interfacial phases.

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