Effects of Ionic Doping on the Behaviors of Oxygen Vacancies in HfO_2 and ZrO_2: A First Principles Study

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***Abstract*-The effects of metallic ion (Al, Ti, or La) doping in HfO_2 or ZrO_2 on the behaviors of oxygen vacancies (V_O) such as the formation energy, density of states, and migration energy were investigated by using first principles calculations. The calculations show that, 1) the doping causes an upward shift of deep V_O levels; 2) dopant radius has a weak impact on the relaxed formation energy of V_O (E^v_f) but a significant impact on the unrelaxed E^v_f ; 3) the relaxed formation energy E^v_f of V_O is remarkably reduced by trivalent ion (Al or La) doping compared to by tetravalent ion (Ti) doping; 4) Al, Ti, or La doping impacts the migration barriers of V_O along different directions.**

Keywords: Hafnium Oxide, Zirconium Oxide, First Principles Calculation, Ionic Doping Effect, Oxygen Vacancy

Introduction

Hf- or Zr-based oxides have been extensively studied for the application in advanced CMOS logic and memory devices [1-3]. It has been demonstrated that the critical device behaviors such as the reliability and work function tuning of high-k/metal gate stacks or the switching behaviors of metal-oxide based resistive random access memory (RRAM) are correlated with the intrinsic oxygen vacancies (V_O) in HfO_2 or ZrO_2 [1-4]. Understanding the doping effects on the behaviors of V_O in HfO_2 and ZrO_2 may help to fundamentally understand the doping effect on the device behaviors,which is crucial for the applications of Hf- or Zr-based oxides in high-k/metal gate stacks and RRAM. In this paper, the behaviors of V_O such as the formation energy, density of state, and diffusivity in pure and Al-, Ti-, or La-doped HfO_2 and ZrO_2 were investigated based on the first principles calculations.

Computational Methods

The density functional theory (DFT) calculations were carried out by using a generalized gradient approximation (GGA) for the exchange-correlation potential and Vanderbilt-type ultrasoft pseudopotentials as implemented in the CASTEP code [5]. A supercell of monoclinic HfO_2 or ZrO_2 containing 96 atoms was constructed. The oxygen atoms in monoclinic HfO_2 or ZrO_2 are either threefold or fourfold coordinated, leading to two kinds of V_O configurations as shown in Fig. 1.

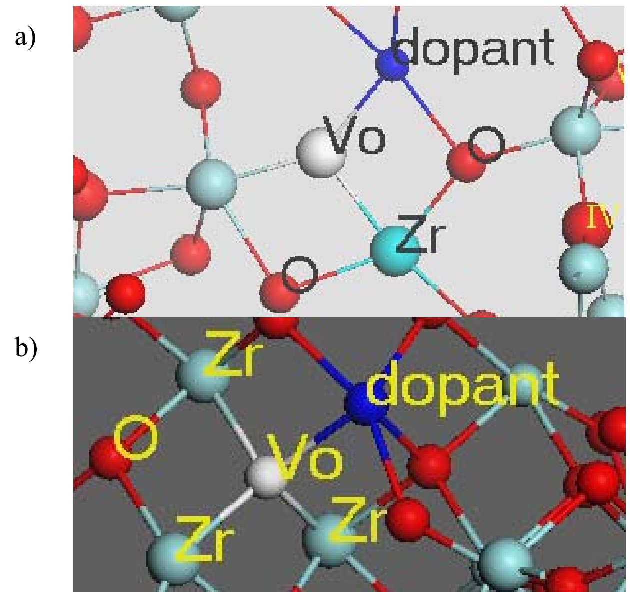

Fig1. Schematic views of three coordinated (a) and four coordinated (b) oxygen vacancy (V_o) at nearest neighboring (NN) position to the dopant.

In the calculations, the V_O properties were simulated by removing one oxygen atom from the supercell and the doping effect was investigated by using a dopant to replace a Hf or Zr atom. Because threefold coordinated vacancy binding with dopant forms relatively stable configuration [6], this work focuses on the three coordinated vacancy. The geometry optimization was performed to relax atoms by fixing the total volume. The V_O formation energy is defined as

$$E^v_f = E_{vac} - E_{free} + \mu_O,$$

where E_{vac} and E_{free} denote the total energy of the supercell

with and without a V_O in the nearest neighbor (NN) of the dopant, respectively. μ_O is the chemical potential of O, and it is half of the oxygen molecule energy in this calculation. The relaxed or unrelaxed V_O formation energy corresponds to the energy with or without lattice relaxation. To simulate the vacancy diffusion in ZrO_2, one oxygen ion is moved from the lattice site to the neighboring vacant sites.

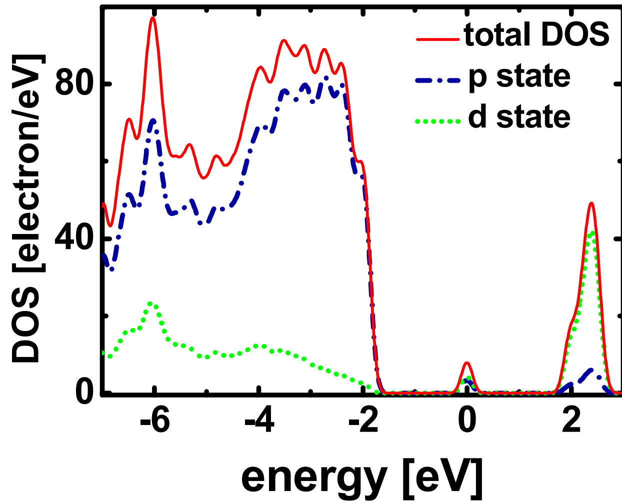

Fig2. Density of state (DOS) of HfO_2 with V_o. The Fermi Level is at 0eV.

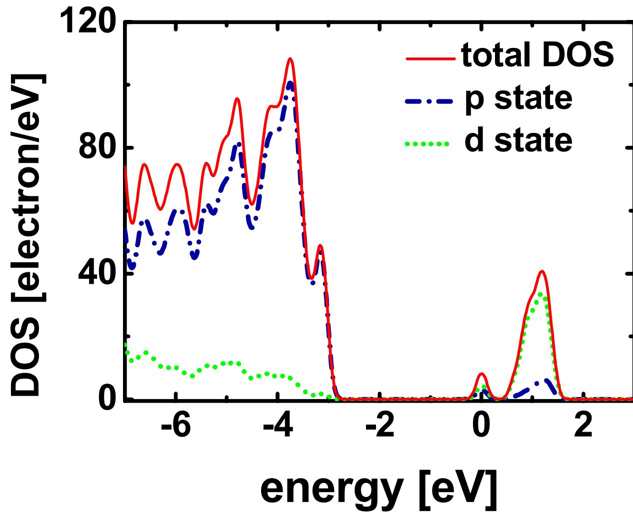

Fig3. DOS of Al doped HfO_2 with V_o at the NN position to the dopant. The deep level is shifted upward, leading to shallow level.

The migration barrier (E_m) is defined as the total energy difference between saddle point energy of the migration process and the energy of the V_O at the initial site [7]. Transition state search is used to calculate E_m. The electron wave functions are described within a plane-wave basis set with an energy cutoff of 300eV. Brillouin Zone (BZ) is sampled at the Γ point. Geometry optimizations are performed until atomic forces are smaller than 0.03eV/ Å. Linear Synchronous Transit (LST), followed by repeated conjugate gradient minimizations and Quadric Synchronous Transit (QST) maximizations calculations are performed to search the saddle point in the V_O migration process.

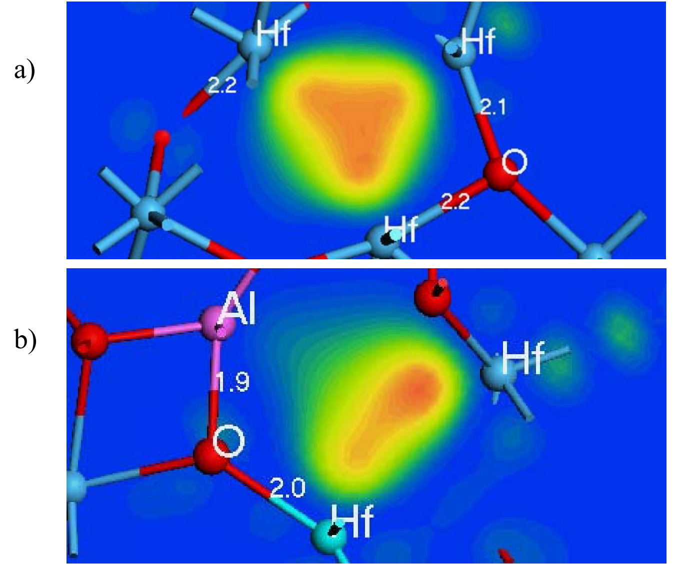

Fig4. Wave function contour plot corresponding to the gap-state at V_o site in undoped (a) and Al doped HfO_2 (b). The localized gap state is mainly contributed from the d states of Hf.

Results

Figure 2 shows the density of states (DOS) of HfO_2 with V_O. The calculated band gap is about 3.3 eV, which is consistent with other DFT calculations [8, 9]. It should be noted that the calculated data is smaller than the experimental data of 5.68 eV [10] due to the well known band gap underestimations of DFT calculations [8]. Fermi level is at mid-gap state, indicating that the defect level of the neutrally charged V_O is occupied. Contour plot of wave function corresponding to the band gap state reveals that electrons are localized around the V_O site (Fig. 4), forming a deep level trap state. The charged traps by electrons or holes will cause the reliability degradation. The localized state of V_O in ZrO_2 is also in the band gap but close to the conduction band (CB). The calculated E^v_f are 5.76 eV and 6.11 eV for HfO_2 and ZrO_2 respectively, consistent with other publications [8, 9].

In the Al-doped HfO_2, the deep trap level is shifted upward to a shallow level, as shown in Fig. 3. In contrast to this, the deep trap level still remains near the mid-gap in the La-doped HfO_2. Since deep level states more easily trap electrons or holes than shallow level, Al- and La-doping HfO_2 can cause different reliability characteristics [11].

Figures 5 and 6 show that E^v_f is remarkably reduced by 2 eV in Al- or La-doped HfO_2 or ZrO_2, while slightly reduced in

the Ti-doped counterparts. This could be owed to major physical origin for the significant decrease of forming voltage in Al doped HfO_2 RRAM [12], as the forming process is interpreted to be equivalent to the dielectric soft breakdown accompanying with creation of V_O. The decrease of E^v_f can be explained based on the effects of Coulomb interactions and lattice relaxation. Trivalent Al or La ion replacing tetravalent Hf or Zr ion forms an acceptor in HfO_2 or ZrO_2 [6].

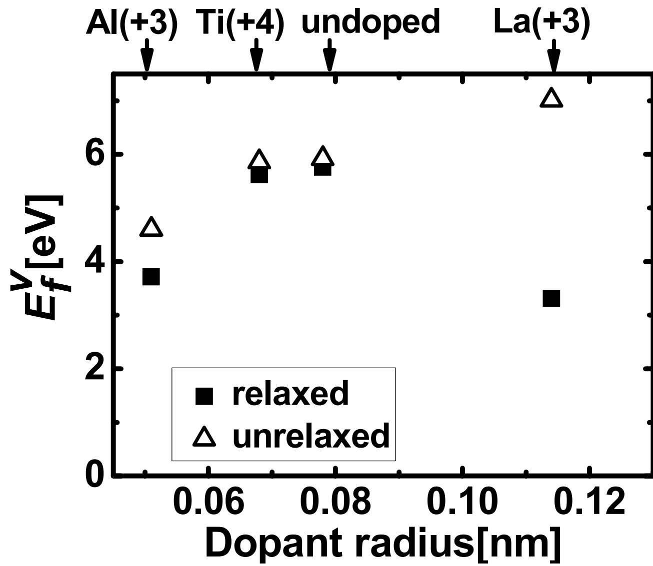

Fig5. The relaxed and unrelaxed V_o formation energy of doped and undoped HfO_2. Trivalent ions significantly reduce the relaxed E^v_f. The unrelaxed E^v_f is increased with the dopant radius.

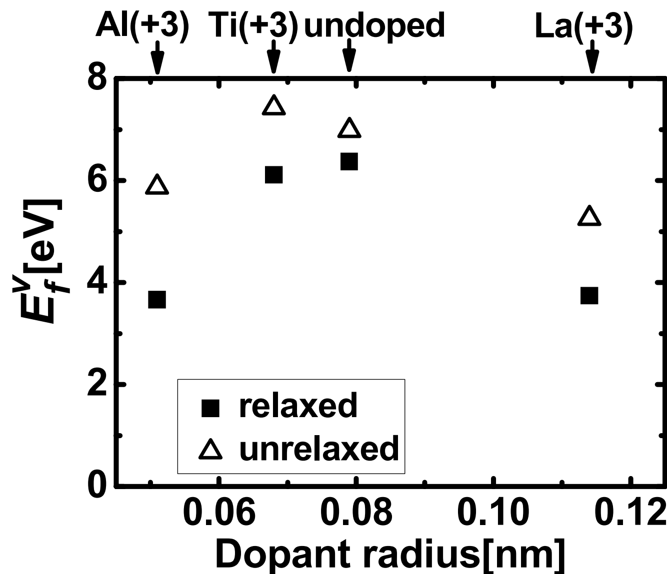

Fig6. The relaxed and unrelaxed V_o formation energy of doped and undoped ZrO_2. Trivalent ions reduce the E^v_f significantly. The unrelaxed E^v_f is also reduced by the trivalent dopant.

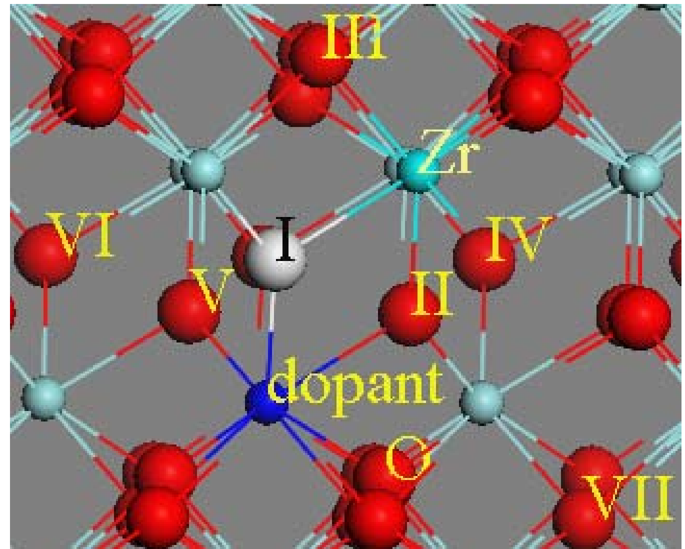

Fig7. Different oxygen sites in the monoclinic ZrO_2 corresponding to possible V_o sites (white), labeled by capital letters. V_o can be separated or be NN to the dopant.

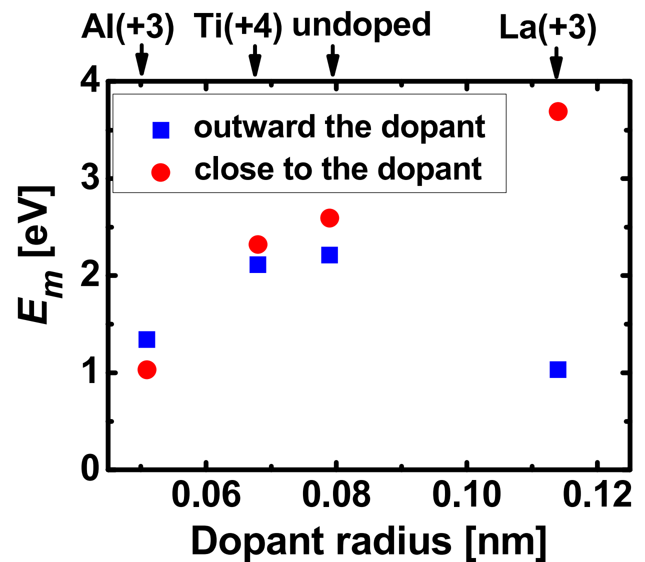

Fig8. The migration barrier (E_m) for V_o or oxygen to migrate close to the dopant and the minimum E_m for V_o to migrate outward to the dopant (migration path from I to III in Fig7).

The localized electrons in the V_O site can be excited and delocalized, leading to the V_O being positively charged. Therefore, the negatively charged trivalent ion (as the ionized acceptor) will tend to combine with the positively charged V_O (as the ionized donor), resulting in decrease of the total energy. This is consistent with the decrease of unrelaxed E^v_f in Al-doped HfO_2 and ZrO_2 and La-doped ZrO_2. In addition to this, dopant with smaller ion radius (like Ti) benefits the lattice relaxation when the vacancy is formed. From analysis of DOS of HfO_2 with V_O, the localized electrons will partly occupy the 5d states of Hf atoms, leading to the neighboring

Hf^{4+} transforming into Hf^{3+} ions, with ion radius increased. In ZrO_2, similarly in HfO_2, when V_O is formed, the neighboring Zr^{4+} will also transform into Zr^{3+}. This will cause the lattice distortion. Doping of smaller radius ions than Hf and Zr like Ti and Al causes the decease of the energetic cost of these distortions. This can account for the decrease of E^v_f in Ti-doped HfO_2. We also notice that the unrelaxed E^v_f in La-doped HfO_2 is increased while the relaxed E^v_f is decreased compared to the undoped HfO_2. The relaxation energy is more than 3 eV. The large relaxation energy is due to the different structures between La_2O_3 and HfO_2, in which the coordination number of cation is different.

The E_m with different migration paths of V_O in ZrO_2 is evaluated, considering the unequivalence of the three coordinated V_O and four coordinated V_O in monoclinic ZrO_2. Figure 7 shows the different locations of V_O with respect to the dopant. V_O can be NN to the dopant or be separated from the dopant. The migration of V_O (equivalent to the oxygen moving in the opposite direction) can thus be classified as migration close to or outward to the dopant. The calculated values of E_m are presented in Table I with different paths indicated by the initial and final V_O locations indicated in Fig.7. For migration of V_O or oxygen close to the dopant, the E_m increases with dopant radius. It can be explained by the fact that oxygen atom is less favorable to pass through the saddle point near the large cation. In contrast to this, the minimum E_m for V_O to migrate outward to the dopant (oxygen to migrate oppositely toward the dopant) decreases when trivalent Al or La is doped, and slightly decreases when Ti is doped, as shown in Fig. 8. This can be attributed to the large lattice relaxation in Al- and La-doped ZrO_2. The relaxation energy of Al- and La-doped ZrO_2 is larger than that of Ti-doped and undoped ZrO_2. Thus, relaxation may facilitate oxygen atom to move in a certain direction. It is also noticed that the migration path with the minimum E_m is the same for Al-, Ti- and La-doped and undoped ZrO_2. Therefore, the minimum migration E_m of V_O is decreased by Al and La dopant.

Conclusion

First principles calculations were performed to investigate the doping effects of trivalent (Al or La) or tetravalent metal atoms (Ti) incorporating into HfO_2 or ZrO_2 on the formation energy, DOS, and migration barrier E_m of V_O. It has been presented that V_O formation energy is decreased by doping trivalent Al and La in HfO_2 or ZrO_2. Al doping also causes the shift of V_O from the deep trap level to shallow level. Al, Ti, or La doping impacts the migration barriers of V_O along different directions and the minimum E_m of V_O among the migration barriers outward to the dopant is decreased. The calculations will help to understand the physical origins of the ionic doping effects on the V_O and to seek the effective path to control the device characteristics.

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Table I. The migration barrier of oxygen or V_o between the neighboring sites in ZrO_2. The capital letters indicate the lattice O sites of the lattice, corresponding to the labels in Fig. 7. N_{Zr} denotes the atom number of Zr or dopant facing both the initial and final V_o sites.
*minimum E_m of V_o migration outward to the dopant (Oxygen toward the dopant).

Vacancy Transition		Migration Path type	N_{Zr}	E_m(eV)			
From	To			Undoped	Ti	La	Al
I	II	Close to the dopant	2	2.59	2.32	3.69	1.03
V	VI	outward dopant	2	3.58	3.26	2.16	1.66
II	IV	outward dopant	1	2.53	2.41	1.61	2.18
I	III	outward dopant*	2	2.21	2.11	1.03	1.34
II	VII	outward dopant	1	2.78	3.10	1.82	3.26