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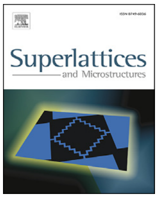

First principles study of defects in high-*k* HfO_2

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ABSTRACT

Intrinsic defects and doping N, Si, Al, and Ta defects in monoclinic HfO_2 were investigated by using the first-principle calculations based on density functional theory (DFT). The results show that the defects of Ta_{Hf}^{+1}, Al_{Hf}^{-1}, V_{Hf}^{-4} are stable under oxygen-rich conditions; while the Hf_i^{+4}, V_{O3}^{+2}, N_{O4}^{-1} are stable when the conditions are hafnium-rich. It is revealed that the defects under hafnium-rich conditions are easy to form, and the results also show the properties of negative $-U$. Defects of the thermodynamic transition levels in the Si band gap can capture or release the charge. It will result in the effect of Fermi level pinning, so it can seriously affect the stability of the device.

1. Introduction

As the traditional metal-oxide-semiconductor field-effect transistor (MOSFET) gate dielectric material, SiO_2 generally produces a large tunneling current, which will be detrimental to the devices [1]. To overcome this difficulty, it is necessary to replace the SiO_2 with an alternative, high dielectric constant (k) oxide. The higher k of the oxide allows us to use a physically thicker layer of this oxide but with the same capacitance per unit area (electrical thickness) as that required of SiO_2, in order to reduce the tunneling current, and to ensure that sufficient drive current [2].

Hafnium dioxide has been proven to be one of the most promising high-k dielectrics because of its high heat of formation and good thermodynamic stability when in direct contact with Si, high k value, wide band gap (>5 eV), right between the silicon conduction band offset [3]. In 2004, X. Wang [4] successfully developed the hafnium compounds as MOSFET gate dielectric layer, and the experimental data reveals that the MOSFET device performance is very good. High k HfO_2 dielectric materials have been successfully applied 45 nm technology and an equivalent thickness of 1.9 nm HfO_2 films have been successfully developed [5]. Compared with SiO_2, HfO_2 suffers from greater defect concentration, which cause high density of charge traps, transient instability of the gate threshold voltage, coulomb scattering of carriers in the substrate channel, instability of the source-level voltage. It is meaningful to study the HfO_2 with some defects.

First principle is an important research method in material field. Its reliability has been proved by many studies [6–8]. Now many researchers study the HfO_2 using first principle calculations. J. X. Zheng [9] studied the point defect in HfO_2, and calculated formation energy of defects. Z. F. Hou [10] doped Al in monoclinic HfO_2 and studied the electronic structure using

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the first-principle calculations. R. A. Casali [11] studied the HfO_2 with Ta based on first-principle calculations. M. Saitoh [12] investigated the N, Si doped into HfO_2. Although above references showed some elements doping in HfO_2, there is no systematic analysis of various defects in HfO_2.

In this paper, intrinsic defects and doping N, Si, Al, and Ta defects in monoclinic HfO_2 were investigated by using the first-principle calculations. In this paper, we established HfO_2 structure and its doped models, calculated the band structures and density of states (DOS). The formation energies and thermodynamic transition level of defects with different charge states were investigated in oxygen-rich and hafnium-rich conditions, and the easy formation of defects were identified. Thus it can obtain the influence on device performance and provide theoretical basis for excellent electrical properties of high k gate dielectric materials.

2. Theoretical models and computational methods

In this paper, the band structure and density of states (DOS) in monoclinic phase of HfO_2 were calculated firstly. The primitive cell of HfO_2 [13] (Fig. 1) contains 12 atoms including 4 Hafnium atoms and 8 oxygen atoms. The Hafnium atoms exhibit a sevenfold-coordination, and there are two kinds of oxygen atoms which exhibit threefold or fourfold coordination.

Our calculations are based on density functional theory (DFT) using the projector augmented wave (PAW) methods, as implemented in the *Vienna ab initial* simulation package (VASP). The exchange-correlation interactions were treated by the generalized gradient approximation (GGA). The valence electrons for hafnium are $5p^6 5d^2 6s^2$ and oxygen is $2s^2 2p^4$. The Cutoff energy is 400 eV. The supercell of the perfect HfO_2 is constituted 12 atoms. Defect calculations are performed in a $2 \times 2 \times 2$ supercell with 96 atoms. Dopants are introduced by substituting one Hf atom by one Si, Al, or Ta atom, and labeled as Si_{Hf}, Al_{Hf}, Ta_{Hf}, respectively. And the three and four-coordinate O substitute N were labeled as N_{O3} and N_{O4}, respectively. While V_{O3} or V_{O4} represent oxygen vacancies with three or four-coordinate in HfO_2. O_{Hf} represent that one Hf substitute one O, Hf_{O3} or Hf_{O4} represent that three or four-coordinate O substitute Hf, respectively. Insert one O or Hf in HfO_2 were labeled as O_i or Hf_i, respectively. The irreducible Brillouin-zone sampling were $2 \times 2 \times 2$. The energy convergence limit is 10^{-4} eV for the electronic loops and 10^{-3} eV for the ionic loops.

2.1. Defect formation energy

The formation energies of defects in HfO_2 were calculated, and the formation energy with a charge state q is given by the following [14,15],

$$E_f = E_{\text{tot}}(\text{defect} : q) - E_{\text{tot}}(\text{perfect}) - \sum_i n_i \mu_i + q\left(\varepsilon_f + E_{\text{VBM}}\right) \tag{1}$$

Where E_{tot} represent total energy, $E_{\text{tot}}(\text{defect}{:}q)$ is the total energy of the HfO_2 containing a defect in a charge state q. $E(\text{perfect})\text{tot}$ is the total energy of the perfect HfO_2. i is species of atoms, n_i is the changes for the number of i atom (added is positive, removed is negative), μ_i is the chemical potential, ε_f is the Fermi level, E_{VBM} is the top of the valence energy value in defective system.

However, it is expected that the calculated E_{VBM} value of the defect HfO_2 differs from that of the perfect HfO_2. This is due to the fact that the defect causes significant distortion to the band structure around the band gap. In this case, it is necessary to determine E_{VBM} [16] of the defective HfO_2 and to line up band structures of the perfect and defective HfO_2. Then the potentials at a number of atomic sites were averaged, and the difference in the averaged potentials (V_{av}) between the perfect and defective HfO_2 was used to determine E_{VBM} of the defective s HfO_2 as follows,

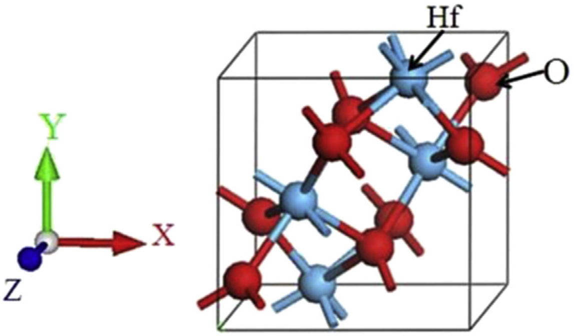

Fig. 1. Monoclinic HfO_2 primitive cell.

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