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Native defect formation and migration in monoclinic zirconium dioxide

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ABSTRACT

We investigate native defect formation and migration in monoclinic zirconium dioxide using first-principles calculations based on density functional theory. The formation energies and transition levels of the native defects can be accurately described by employing nonlocal B3LYP hybrid functional. This methodology overcomes the band-gap problem in traditional functionals and renders the approach more predictive. By band alignments between the GaAs and the ZrO_2, we are able to determine the position of defect levels in the GaAs relative to the ZrO_2 band gap and assess how they will affect the device performance. In addition, we also investigate diffusions of neutral and charged defects in ZrO_2. It is found that O_i is the one with the lowest migration barrier. Hence, this point defect is identified most dangerous in monoclinic ZrO_2 within the context of high-k gate dielectric application.

1. Introduction

High permittivity gate dielectrics have been attracting considerable attention since silicon dioxide is reaching its fundamentally physical limit in metal oxide semiconductor field effect transistors (MOSFETs) [1–3]. In order to maintain the leakage current across a very thin gate oxide at a relatively low level, dielectrics with higher dielectric constant have to be explored to integrate into the devices. Zirconium oxide based gate dielectrics are very promising candidates for their high permittivity and good thermodynamic stability with some semiconductors [4–6]. An atomic layer deposition (ALD) technique becomes a dominating deposition method for high k dielectrics because of its superior ability to deposit uniform films over larger areas with precise thickness control [7]. Pure zirconia can exist in three different thermodynamically stable polymorphs at atmospheric pressure: a monoclinic phase at low temperature with space group of P21/c, a tetragonal phase at temperature of 1400 °C with space group of P42/nmc, and a cubic phase at temperature above 2600 °C with space group of Fm3m [8]. The monoclinic phase is usually the most stable at room temperature.

Several theoretical studies on the defect formation energies and transition levels in zirconia have been carried out. Foster et al. [9] studied formation energies and their energy levels of oxygen vacancies (V_O) and oxygen interstitial (O_i) in monoclinic zirconia. However, their studies did not consider the chemical potential and Fermi level as controlling variables for the formation energies. Zheng et al. [10] found that V_O and O_i in ZrO_2 show negative-U behavior. When the Fermi level is constrained to be within the band gap of silicon, the dominant defects are negatively charged zirconium vacancies (V_{Zr}). However, they carried out the calculation using generalized gradient approximation (GGA), which is known to underestimate the band gap. The error leads to larger uncertainties in defect formation energies and transition levels. Yu et al. [11] also investigated formation energies of native defects in ZrO_2

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using density functional theory with the GGA method. They suggested that V_O and V_{Zr} vacancies are dominant defects in ZrO_2. Their results also require some interpretations because their calculation underestimates the band gap of ZrO_2. Van de Walle et al. [12] studied native defects in ZrO_2 using the hybrid functional developed by Heyd, Scuseria and Ernzerhof (HSE). The calculated band gap is 5.22 eV for ZrO_2, which is in very good agreement with the experimental values. They investigated formation energies and transition levels of native defects in ZrO_2. However, their studies did not consider the position of defect levels in the GaAs relative to the ZrO_2 band gap. The impact of native defect on device performance is still a subject of much debate [13–17].

Besides knowing their electronic properties, it is also important to know how native point defects migrate in the crystal lattice. Knowledge of migration of point defects greatly contributes to the understanding of their incorporation during growth and processing. Information about diffusion or migration of the defects in ZrO_2 is currently limited.

Here we use the first principles calculations to determine the formation energy and transition levels of native defects in zirconia. Our calculations are based on density functional theory and B3LYP hybrid functional, which overcomes the traditional problem of underestimation of band gap in DFT using LDA or GGA exchange functional. The method thus allows us to obtain the accurate position of defect levels relative to the semiconductor band gap. This allows us to assess whether these defects will act as sources of fixed charge or carrier traps. In addition, we investigate defect diffusion. Migration barriers of the native defects are discussed. We hope that our work can contribute to the applications of ZrO_2.

2. Method of calculations

The calculations are performed using the CASTEP code. $2\times2\times2$ monoclinic ZrO_2 periodic cells are chosen to represent the gate dielectric in our calculation. The large cell separates the period image of defects by a distance larger than 10 Å and makes sure that interaction between defects is eliminated. We investigate the formation energies, band structure and density of states using nonlocal hybrid B3LYP functional, which gives a more precise band structure than the local functionals. The valence electron configurations for Zr and O are considered as $4s^24p^64d^25s^2$ and $2s^22p^4$, respectively. The plane wave cutoff energy is set to 700 eV. Due to the larger cell size, only one gamma point is used for the geometry optimization [1]. The Monkhorst-Pack scheme is used for k point sampling with a $2\times2\times2$ mesh for band structure and density of states calculations. In order to examine impacting of lattice parameters on results, we optimize lattice constants of monoclinic ZrO_2 using GGA functional, its values of $a=5.181$ Å, $b=5.250$ Å and $c=5.354$ Å, which is a little larger than experimental values of $a=5.151$ Å, $b=5.203$ Å and $c=5.316$ Å [18]. The optimized and experimental lattice constants are used to investigate formation energy and transition level, respectively. It is found that the discrepancy is less than 0.25 eV for formation energy of neutral defects and 0.04 eV for transition level. The lattice constants calculated by nonlocal B3LYP hybrid functional are close to experimental values compared to local GGA or LDA functional. Therefore, the error is smaller for B3LYP hybrid functional than the local functional. The small discrepancy will cannot change the final result. Therefore, we fix the lattice constants with experimental values during the calculation. The internal coordinates are fully relaxed during geometry optimization. The optimization will finish if the convergence criteria is satisfied (maximum force between atoms is 0.01 eV/Å. Maximum displacement is 10^{-3} Å. Maximum energy change is 10^{-5} eV/atom). Fig. 1 shows the band structure and density of state of monoclinic ZrO_2. It is found that the band gap of monoclinic ZrO_2 is 5.419 eV, which is in good agreement with the experimental value of 5.0–5.8 eV [19]. The valence band is mainly composed of O 2s, O2p, Zr 4p and Zr 4d. However, upper valence band is essentially determined by O 2p and Zr 4d. It is observed that O 2p hybridizes with Zr 4d. Valence band maximum (VBM) and conduction band minimum (CBM) are determined by O 2p and Zr 4d, respectively. In this paper, migration of native defects is investigated using local density approximation (LDA) of CA–PZ.

3. Results and discussion

3.1. Formation energies and transition levels of native defects

We investigate the formation energies of native defects in ZrO_2, including oxygen vacancy (V_O), zirconium vacancy (V_{Zr}), oxygen interstitial (O_i) and zirconium interstitial (O_{Zr}). The defect formation energies in compound systems can be obtained from the total energy calculation of the supercell [20]

$$\Delta H_f(a,q)=\Delta E(a,q)+\sum_{\alpha} n_a\Delta\mu_\alpha+qE_{\mathrm{F}} \tag{1}$$

$$\Delta E(a,q)=E(a,q)-E(\mathrm{ZrO_2})+\sum_{\alpha} n_\alpha\mu_\alpha+q(E_{\mathrm{v}}+\Delta V) \tag{2}$$

where $E(\alpha,q)$ is total energy for ZrO_2 supercell containing the relaxed defect α in the charge state q. $E(ZrO_2)$ is the total energy for the same ZrO_2 supercell in the absence of defect. n_α is the number of atoms for each defects. E_v represents the energy of the valence band maximum of the defect free system. ΔV represents the shift of VBM in a defect supercell, which is usually negligible in the calculation [21]. $\Delta\mu_\alpha+\mu_\alpha$ is the absolute value of the chemical potential of atom α. μ_α is the chemical potential of the element. $\Delta\mu_\alpha$ is the relative chemical potential. To keep the ZrO_2 thermodynamically stable, it also requires to satisfy: $\Delta\mu_{Zr}+2\Delta\mu_O=\Delta H_f(ZrO_2)$, where ΔH_f is enthalpy of formation of ZrO_2. Table 1 shows calculated and experimental band gap and enthalpy of formation for monoclinic ZrO_2. Our calculated value is $\Delta H_f(ZrO_2)=-12.262$ eV for a B3LYP method (experiment: -11.407 eV, Ref. [22]). The results are also compared with GGA and LDA methods. The oxygen and zirconium rich limit is determined by $\Delta\mu_O=0$ and $\Delta\mu_{Zr}=0$, respectively.

Fig. 2 shows formation energies with respect to the Fermi level which change from VBM to CBM. For each defect in ZrO_2, only the charge state that gives the lowest