Impact of La Doping on the HfO_2 Gate Stack Reliability via First-Principles Simulation

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Low threshold-voltage n-MOSFETs have been successfully realized through the incorporation of La into the Hf-based high-k gate stack[1]. However, the impact of La doping on the gate stack reliability is still not well understood. For instance, as compared to an undoped HfO_2 gate stack, the PBTI performance of a La-doped gate stack is improved under low oxide stress field but TDDB is degraded under higher oxide stress field[2,3]. Some simulation studies have attributed the improvement to the suppressed formation of oxygen-vacancy (V_O) defects by La doping[4,5]. But it is unclear why the La-doped gate stack is in turn more susceptible to defect generation under higher oxide stress field[2,3]. A recent study[6] also showed a retardation of PBTI recovery in the La-doped HfSiON gate stack, implying that La doping gives rise to a greater number of deep electron traps. Thus, it is crucial for one to gain a sound understanding on the effect of La doping on the reliability of Hf-based gate stacks. In this paper, we examine the influence of La on the properties of the V_O defect in the HfO_2 via first-principles simulation.

The supercell used in our simulation study was amorphous HfO_2, consisting of 32 Hf atoms and 64 O atoms, with a density of 9.68 g/cm^3. The amorphous structure was generated from a cubic HfO_2 structure, via molecular dynamics, following the melt-and-quench scheme[7]. La doping was realized by manually replacing two nearby Hf atoms by La atoms and then allowing the system to relax to the minimum energy state. All calculations were performed using VASP[8] which employs the plane wave pseudo-potential methods within the density functional theory. A hybrid density functional scheme is applied to obtain the correct HfO_2 band gap[9]. The ultra-soft pseudo-potentials were used to represent the interactions between the ion core and the valence electrons. The exchange correlation functional was treated within the GGA of Perdew Burke and Ernzerhof[10]. In all calculations, the cut-off energy and Γ-point were tested. For structure optimization, the conjugate gradient method was used and the ion positions were optimized until the residual force was less than 0.01 eV/Å.

The formation energy E_f of a defect in the HfO_2 was calculated from the total energy E of the defective supercell according to (1):

$$E_f(\alpha,q) = E(\alpha,q) - \left(E_0^0 + n_{Hf}\mu_{Hf} + n_O\mu_O + n_{La}\mu_{La}\right) + q\left(\varepsilon_F + E_{VBM}\right) \quad (1)$$

where E_0^0 is system energy of the defect-free supercell and E_{VBM} is the valence band maximum of HfO_2. For a defect α in charge state q, E_f is a function of the Fermi level ε_F and the respective chemical potential of Hf, O and La, denoted by μ_{Hf}, μ_O, and μ_{La}, respectively. The terms n_{Hf}, n_O and n_{La} represent the corresponding number of Hf, O and La atom(s) added/removed from the supercell to form the defect. The charge transition level (CTL) for neutral-to-negative state transition of the V_O defect is also calculated and is given by the ε_F which corresponds to $E_f(\alpha, q) = 0$. The 0/– CTL, measured with respect to E_{VBM}, is akin to the trap level of the V_O defect in the HfO_2 bandgap[9].

The first part of our study is focused on the V_O defect. The O atom between the two La atoms was manually removed to generate the V_O defect (Fig. 1). The structure was then relaxed under both the neutral and single negative-charge state until the respective minimum energy state was attained. The resultant E_f of the neutral V_O defect is –3.78 eV, substantially lower (negative in fact) as compared to the E_f of +5.85 eV for an undoped HfO_2. This is contrary to the finding of ref. (4) and (5), which reported an *increase* of V_O formation energy by ~0.7 eV in the La-doped HfO_2. We believe the discrepancy is due to the fact that the value reported in ref. (4) and (5) is for the formation of a second V_O defect in the supercell, as two O atoms were removed in the calculation. In our case, we consider only the first V_O defect formation; the negative E_f means that our structure is energetically more favorable compared to those considered in ref. (4) and (5). The substantially reduced E_f implies a greater density of V_O's in the La-doped HfO_2, and given that the CTL is comparable to that in the undoped HfO_2 (Fig. 2), the PBTI performance should be degraded. Hence, the improved PBTI performance of the La-doped HfO_2 at low oxide stress field[2,3] is most likely due to the reduced gate current, as a result of the increased tunneling barrier induced by La dipoles at the HfO_2/SiO_x interface[2], and not because of suppressed V_O formation. It should also be noted that the V_O defect in both the La-doped and undoped HfO_2 is a very shallow electron trap and could not account for the reduced long-term PBTI recovery[6].

Considering the ease of V_O formation in the La-doped HfO_2, we also examine the possible formation of the V_O-O_i (where O_i denotes an interstitial oxygen atom) defect pair (Fig. 3), for 3 arbitrarily chosen O_i positions in the vicinity of the V_O site. The E_f, ranging from –2.7 to –2.9 eV, is higher than that of the single V_O defect but is also significantly lower than the corresponding E_f of the undoped HfO_2, indicating that V_O-O_i defect pairs are also energetically favorable in the La-doped HfO_2. But unlike the case of the V_O defect, the CTL of the V_O-O_i defect pair is much deeper (1.6 to 2.8 eV), with some of these CTLs situated within the Si band gap. This observation implies that the V_O-O_i defect, when formed, may function as an effective trap-assisted tunneling center. This explains the degraded TDDB reliability of the La-doped HfO_2 gate stack[2]. Trap states aligned with the electron Fermi energy would set off a positive feedback cycle that accelerates wear-out and eventually triggers breakdown of the gate stack. Under a moderate positive gate bias, electrons which tunneled in from the Si substrate could be captured at these defect states. Since these defect states are >1 eV below the Si conduction band edge, they function as deep electron traps, i.e. the trapped electrons are not readily emitted when the gate stress voltage is removed. This explains the retardation of PBTI recovery[6]. On the other hand, in the undoped HfO_2, the E_f of the V_O-O_i defect is much higher (6.7 eV) and therefore it is less likely to be formed. Moreover, the CTL is deep – located in the HfO_2 valence band – meaning that the defect, even if present, does not function as an electron trap under PBTI stressing.

References: [1] Kirsch *et al.*, *IEDM Tech. Dig.*, 370 (2006); [2] Kang *et al.*, *IEDM Tech. Dig.*, 115 (2008); [3] Sato *et al.*, *IEDM Tech. Dig.*, 119 (2008); [4] Umezawa *et al.*, *Appl. Phys. Lett.*, **91**, 132904 (2007); [5] Liu and Robertson, *Appl. Phys. Lett.*, **94**, 042904 (2009); [6] Du *et al.*, *IEDM Tech. Dig.*, 94 (2010); [7] Scopel *et al.*, *Phys. Rev. B*, **77**, 172101 (2008); [8] Kresse and Hafner, *Phys. Rev. B*, **47**, 558 (1993); [9] Alkauskas and Broqvist, *Phys. Rev. Lett.*, **101**, 046405 (2008); [10] Perdew and Burke, *Phys. Rev. Lett.*, **78**, 1396 (1997).

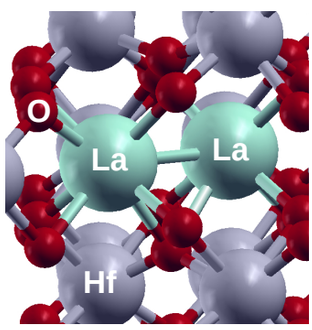

Fig. 1: Atomic structure in the vicinity of an oxygen vacancy defect in a La-doped amorphous HfO_2 supercell. The oxygen vacancy defect is situated in-between the two La atoms as shown.

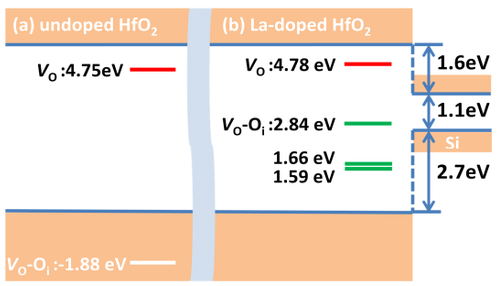

Fig. 2: Schematic energy band diagram illustrating the charge transition level (akin to the trap level) of the oxygen vacancy (V_O) and oxygen-vacancy cum interstitial-oxygen (V_O-O_i) defect in the (a) undoped HfO_2 and (b) La-doped HfO_2.

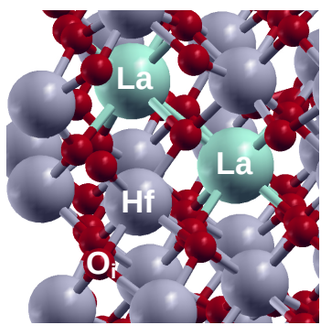

Fig. 3: In forming the V_o-O_i defect pair in the La-doped HfO_2, the O atom in-between the two La atoms is manually removed and placed in an interstitial position in a nearby region, as denoted by O_i. Three arbitrary O_i positions were examined.