Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp732-733

A New Atomic Defect Model for Positive-Bias Temperature Instability in the High-k Gate n-MOSFET

C. J. Gu and D. S. Ang
Nanyang Technological University, School of Electrical and Electronic Engineering
50 Nanyang Avenue, Singapore 639798. E-mail: edsang@ntu.edu.sg

Abstract – We show, from first-principles simulation that the oxygen vacancy (V_O) defect has a shallow trap state (~1 eV below the HfO_2 conduction band edge) and it could not explain the wide spread in electron detrapping time constants observed in the recovery study of positive-bias temperature stressed high-k/metal gate n-MOSFETs. A new atomic model, based on the vacancy-interstitial (V_O-O_i) paired defect, is proposed. Depending on the position of the interstitial oxygen, the trap state of the V_O-O_i defect could vary across the entire band gap of HfO_2, adequately explaining electron trapping at deep states and the prolonged relaxation observed experimentally.

1. Introduction

With the adoption of the high-k/metal gate stack in advanced CMOS technologies, positive-bias temperature instability (PBTI) has emerged as a critical reliability issue for the n-MOSFET. Studies have shown that PBTI arises mainly from electron trapping at high-k bulk defects [1]. Interestingly, study on PBTI recovery has revealed a very wide electron detrapping time constant distribution (~10^{-6} or shorter to 10^5 s or longer), even for ultra-thin high-k oxides (~2-3 nm) [2]. This finding implies that some of the electrons are trapped at deep trap states. Recently, it was observed some of the shallow electron traps could be transformed to deeper traps (hence "locking" in the trapped electrons) during PBTI stressing [3]. However, the nature of the oxide defects remains unclear, although it is widely believed that oxygen vacancies (V_O's) are the main culprits. In this paper, we show via first-principles simulation that the very shallow trap states of the V_O defect is inconsistent with the broad distribution of electron detrapping time constants observed. A new defect model, called the vacancy-interstitial (V_O-O_i) pair is shown to be able to explain the experimental features of PBTI.

2. Computational Method

All calculations are performed using VASP [4], on a 2×2×2 supercell comprising 32 Hf and 64 O atoms. The density of the supercell is 9.68 g/cm^3. An amorphous structure was generated from a cubic HfO_2 via molecular dynamics, following the melt-and-quench scheme [5]. The hybrid scheme is used to correct the band gap [6] so that the trap level could be precisely determined. In all the calculation, the cut-off energy and κ-points were tested. For the structure optimization, the conjugate gradient method is used and the ion positions are optimized until the residual force is less than 0.01 eV/Å. After full structural relaxation, the mean square displacement (MSD) for all the atoms in the negatively charged supercell was extracted relative to the atoms in the neutral supercell. The charge transition level (CTL), which corresponds to the trap energy level (relative to the valence band maximum of HfO_2) for electron capture, was calculated from the difference in the total energy of the negatively charged and neutral supercells [6].

3. Results and Discussion

A. Oxygen Vacancy Defect

A V_O defect was created at each of the 64 O positions by manually removing the O atom (Fig. 1) and then subjecting the defective supercell to full structural relaxation under neutral and negatively charged conditions until the respective minimum energy state was attained. As expected, structural rearrangement occurred upon the capture of an electron (Fig. 2(a)). However, the CTLs for the neutral-to-negative (0/–) transition are very shallow (~1 eV below the HfO_2 conduction band minimum E_C) for all 64 V_O's. It should be mentioned that the same study was carried out on several hundred V_O's in other amorphous supercells and similar results are obtained. The shallow CTLs means that electrons captured at V_O's during PBTI stressing would be spontaneously emitted when the stress is removed, since there is only a small barrier for the trapped electron to escape either to the gate or substrate. Thus, while V_O's could account for the initial (fast) recovery, they fail to explain recovery transient that lasts several tens of thousands of seconds or more even in gate stacks with an ultra-thin HfO_2 (~2 nm) layer [2].

B. Vacancy-Interstitial Paired Defect

The ionic nature of HfO_2 and electron spin resonance measurement result showing the presence of not only vacancies but also interstitial O atoms prompted us to examine the vacancy-interstitial (V_O-O_i) pair as a possible defect for PBTI. It should be noted that the existence of O_i alone is deemed not likely in view that high-k oxides are generally O deficient. To simulate the formation of the V_O-O_i paired defect, an O atom was moved out of its lattice position and placed in an interstitial position (Fig. 3). A total of 10 arbitrarily chosen O_i positions in the vicinity of a given V_O site were studied. Unlike the case of the V_O-only defect for which the CTL is distributed narrowly above the $E_{C,Si}$ (Fig. 2(b)), the CTL for the V_O-O_i paired defect varies broadly, from ~0.7 to 4.8 eV below the HfO_2 E_C (Fig. 4) The deep CTLs (> 2.7 eV) indicate that some V_O-O_i defects could function as deep electron traps. Electrons captured at these deep trap states are not readily emitted when the stress is removed, even in the case of an ultra-thin oxide, due to the appreciable barrier between the trap level and the Si E_C or Fermi level of the gate. The result could therefore explain the long term recovery transient observed experimentally. It should be highlighted that the CTL of a given V_O-O_i paired defect depends on the position of the O_i – certain O_i positions give rise to shallow trap levels while others give rise to much deeper ones. This implies that it is possible for the trap level to change from shallow to deep when the position of O_i is changed, providing a plausible explanation for the recently observed transition from shallow to deep electron trapping during PBTI stress [3]. As can be seen from electron density function analysis, the trap state is shallow when the electron is captured at the V_O site (3*d* orbitals of the Hf atoms are involved) – Fig 5(a) – whereas it is much deeper when the captured electron mainly resides at the O_i (2p orbital of the O_i atom is involved) – Fig. 5(b). For other intermediate trap levels, the captured electron is found to be distributed between the V_O and O_i (not shown). The varying degree of interaction between V_O and O_i is believed to have given rise to the broad trap-level distribution.

4. Summary

First-principles simulation shows that the V_O defect is a very shallow electron trap and it could not account for the very long time constants for electron detrapping revealed in PBTI recovery measurement. Study on an alternative V_O-O_i paired defect model shows a broad trap-level distribution across the HfO_2 bandgap, depending on the position of the O_i. The results show that the V_O-O_i paired defect could explain long term PBTI recovery transient as well as the transition of shallow to deep electron trapping during PBTI stressing.

References: [1] Bersuker *et al.*, *IEEE Trans. Dev. Mat. Reliab.*, vol. 7, p. 138, 2007; [2] Zhao *et al.*, *IEEE IRPS*, p. 50, 2010; [3] Gao *et al.*, *IEEE Electron Dev. Lett.*, vol. 34, p. 351, 2013; [4] G. Kresse and J. Hafner, *Phys. Rev. B*, vol. 47, p. 558, 1993; [5] Scopel *et al.*, *Phys. Rev. B*, vol. 77, 172101，2008; [6] Alkauskas *et al.*, *Phys. Rev. Lett.*, vol. 101, 046405, 2008.

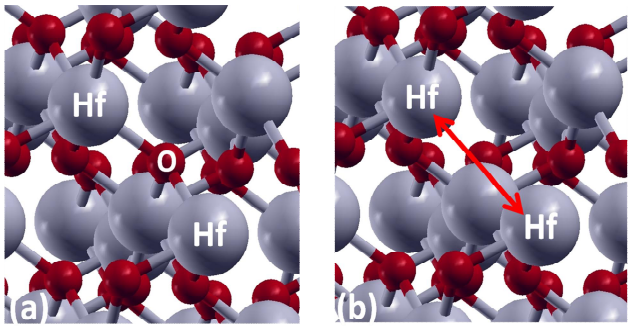

Fig. 1. (a) Ball and stick diagram of part of the defect-free amorphous HfO_2 supercell used in our simulation study. (b) The O atom in between the two Hf atoms (as labeled in (a)) was manually removed and then the supercell subjected to full structural relaxation to create an oxygen vacancy (V_O) defect.

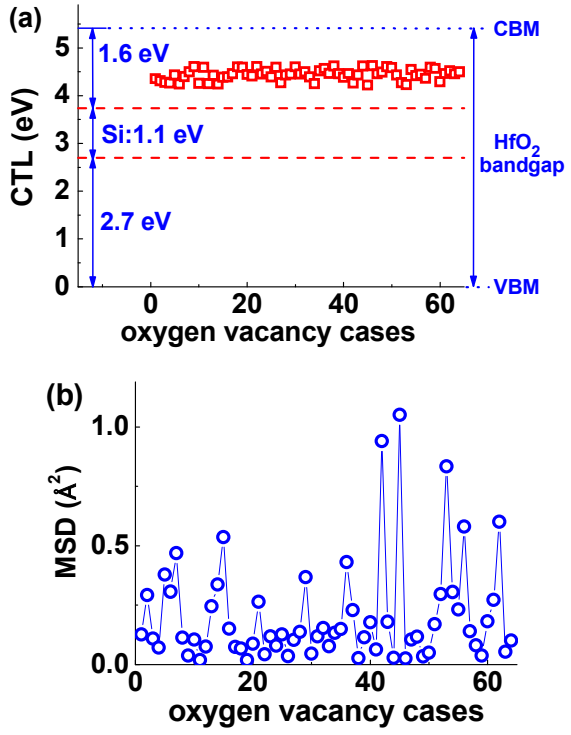

Fig. 2. (a) Charge transition level (for neutral to negative) for all 64 cases of oxygen vacancy defect in an amorphous HfO_2 supercell. CTL = 0 eV corresponds to the valence band maximum (VBM) of HfO_2; the conduction band minimum (CBM) is denoted by the upper dotted line. The upper (lower) dashed line delineates the conduction (valence) band offset between HfO_2 and Si. (b) The corresponding mean square displacement (MSD) of all atoms in the negatively charged supercell. The MSD is measured with respect to the atom positions in the neutral supercell. The line serves as an eye-guide only.

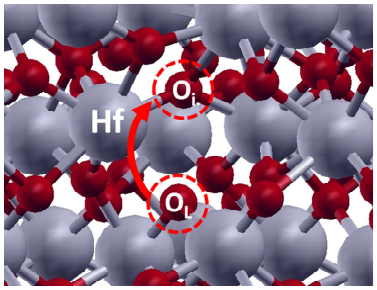

Fig. 3. An illustration of the formation of a vacancy-interstitial (V_O-O_i) paired defect in an amorphous HfO_2 supercell. An O atom, denoted as O_L, was removed from a lattice site and placed in a nearly interstitial position (void), denoted as O_i and the resultant supercell subjected to full structural relaxation. In some cases, the O_i is found to return to its original position (i.e. O_L) after structural relaxation, implying that the V_O-O_i defect formed is unstable.

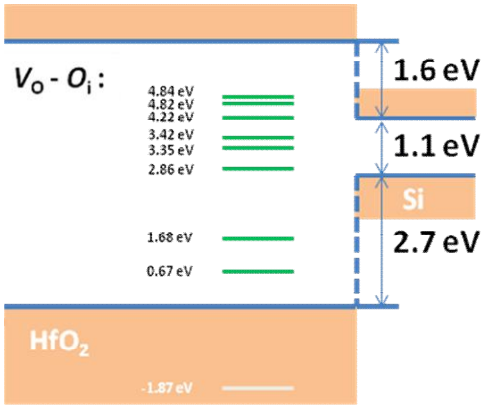

Fig. 4. Charge transition level (neutral-to-negative) for several arbitrarily chosen interstitial O (O_i) atom positions around a given vacancy (V_O) defect. A broad trap distribution, ranging from ~0.6 to 4.7 eV below the HfO_2 conduction band minimum is apparent. For a particular case, the CTL is located in the HfO_2 valence band.

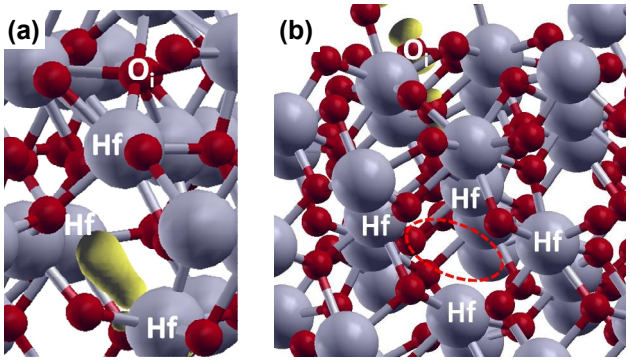

Fig. 5. An indication of how the additional electronic charge (yellow shades) is distributed in the vicinity of a *negatively charged* V_O-O_i defect: (a) Shallow CTL (1.3 eV below the HfO_2 CBM) – the electronic charge resides primarily at V_O, i.e. the electron is trapped at V_O. (b) Deep CTL (2 eV below the HfO_2 VBM) – the electronic charge resides mainly on O_i i.e. the electron is trapped at O_i (V_O is denoted by the dashed circle). For intermediate CTLs, the additional electronic charge is shared between the V_O and O_i (not shown).