AIP | Applied Physics Letters

H-related defect complexes in HfO2: A model for positive fixed charge defects

Joongoo Kang, E.-C. Lee, K. J. Chang, and Young-Gu Jin

Citation: Appl. Phys. Lett. **84**, 3894 (2004); doi: 10.1063/1.1738946
View online: http://dx.doi.org/10.1063/1.1738946
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v84/i19
Published by the American Institute of Physics.

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT

Downloaded 19 Apr 2013 to 143.248.118.122. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://apl.aip.org/about/rights_and_permissions

HTML ABSTRACT • LINKS

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 19 10 MAY 2004

H-related defect complexes in HfO_2: A model for positive fixed charge defects

Joongoo Kang, E.-C. Lee, and K. J. Chang[a)]
Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

Young-Gu Jin
Computational Science and Engineering Center, Samsung Advanced Institute of Technology, Suwon, Korea

(Received 5 February 2004; accepted 12 March 2004; published online 29 April 2004)

Based on first-principles theoretical calculations, we investigate the hydrogenation effect on the defect properties of oxygen vacancies (V_O) in HfO_2. A defect complex of V_O and H behaves as a shallow donor for a wide range of Fermi levels, with a positive charge state, and this complex is energetically stable against its dissociation into V_O and H. We suggest that the V_O–H complex is responsible for the formation of positive fixed charges, which neutralize negative fixed charges during the postannealing process of SiO_x/HfO_2 stack. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1738946]

Hafnia (HfO_2) and zirconia (ZrO_2) have currently attracted much attention because of the potential use for alternative dielectrics to SiO_2 in metal-oxide-semiconductor (MOS) devices due to their high dielectric constants and good thermal stability in contact with Si.[1] Several experiments have reported that as-deposited SiO_x/HfO_2 (or SiO_x/ZrO_2) gate dielectric stacks on Si exhibit negative fixed charges.[2–5] During the postannealing process in O_2, the density of negative fixed charge defects decreases, while that of interface defects increases.[2–4] When annealing temperatures are above 600 °C, positive fixed charges were shown to appear, particularly in the SiO_x/ZrO_2 stack after the decrease of the negative fixed charge.[2] From the observed correlation between the depassivation of P_{b0} centers and the generation of positive fixed charges, it was suggested that the positive fixed charge may be due to overcoordinated oxygen centers induced by hydrogen during the postannealing process.[2] However, the origin of fixed charge defects has not been resolved yet. The generation of fixed charges within gate dielectrics is one of the critical concerns for fabricating new high permittivity gate stacks. Thus, it is important to understand the origin of fixed charges at the atomic scale to control the density of fixed charges.[5,6]

In this letter, we perform a comprehensive and detailed study of the energetics and the electronic structure of various H-related defects in HfO_2 based on the first-principles calculations. We find that a defect complex consisting of O vacancy (V_O) and H behaves as a shallow donor, whereas an interstitial H is a negative-U defect. The V_O–H complex is energetically more stable than for well separated V_O and H, and remains in a positive charge state for a wide range of the Fermi levels, which covers the band gap of bulk Si. Thus, the formation of the positively charged V_O–H complex is suggested to be responsible for the increase of positive fixed charge defects during the postannealing process.

We use the first-principles pseudopotential method within the local-density-functional approximation (LDA) and the generalized gradient approximation (GGA).[7] Norm-conserving nonlocal pseudopotentials are generated by the scheme of Troullier and Martins[8] and transformed into a separable form of Kleinman and Bylander.[9] For the Hf atom, we include a nonlinear partial core correction[10] for the exchange-correlation functional to deal with the overlap between the core and valence electron densities. The wave functions are expanded in plane waves up to a cutoff of 60 Ry. All the atoms are fully relaxed using the conjugate gradient method. The defect formation energies are calculated for a supercell containing 96 host atoms in monoclinic HfO_2, with choosing the energies of free H_2 and O_2 molecules as the H- and O-chemical potentials, respectively. The details of the calculational method, the accuracy of total energies, and the structural parameters in perfect HfO_2 are given elsewhere.[11]

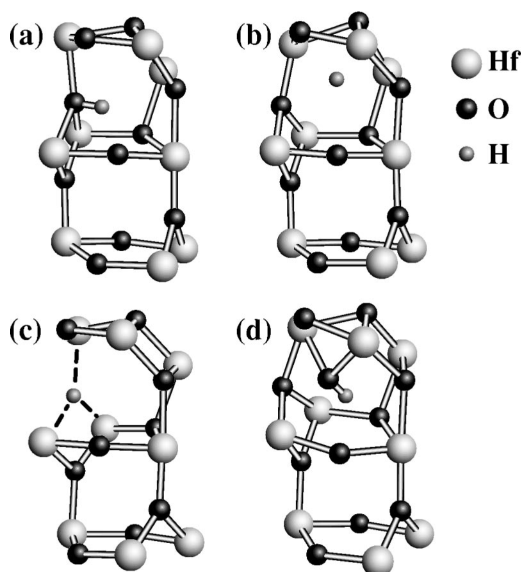

FIG. 1. Atomic structures for H-related defects in HfO_2: (a) H^+ bonded to a threefold-coordinated O atom, (b) H^- at an interstitial site, (c) the V_O–H complex, and (d) the OH unit bonded to two Hf atoms.

a)Author to whom correspondence should be addressed; electronic mail: kchang@kaist.ac.kr

 © 2004 American Institute of Physics

Downloaded 19 Apr 2013 to 143.248.118.122. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://apl.aip.org/about/rights_and_permissions

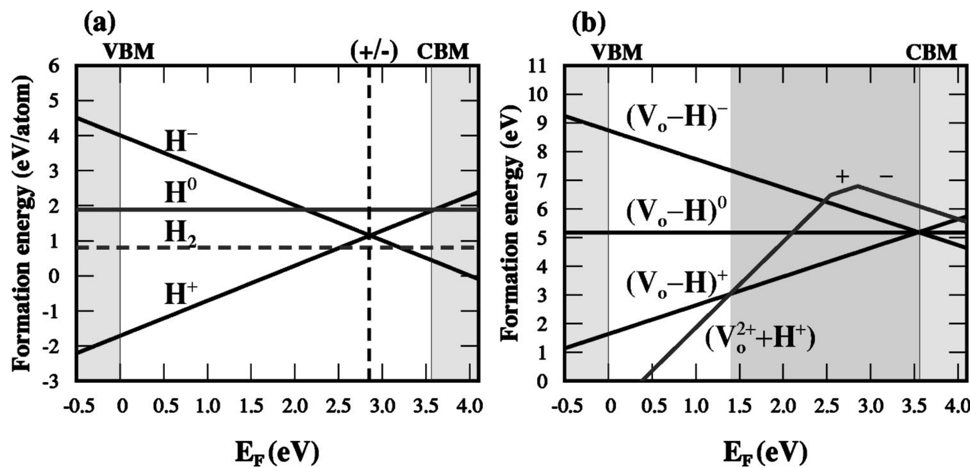

FIG. 2. Formation energies for (a) interstitial H and H_2 molecule, and (b) the V_O–H complex. In (b), the formation energy of well separated V_O and H in each stable charge state is compared with that for the V_O–H complex, and the shaded region indicates the range of Fermi levels in the gap, where $[V_O\text{–H}]^{1+}$ is the most stable defect.

At ambient conditions, HfO_2 has a monoclinic structure with two types of O atoms, which are threefold and fourfold coordinated, while all the Hf atoms are in a sevenfold-coordinated configuration. For a single H impurity in HfO_2, the stable geometry depends on the charge state of the defect. Considering many interstitial positions including antibonding and bond-centered sites, we find that for a positive charge state, H^+ forms a strong bond with a threefold-coordinated O in a manner that the O—H bond is perpendicular to a nearly flat plane consisting of the O and its three neighboring Hf atoms, as shown in Fig. 1(a). The calculated O—H bond length for H^+ is 0.982 Å, which is very close to the bond length of 0.965 Å for a H_2O molecule. When H^+ is bonded to a fourfold-coordinated O, the energy increases by 0.68 eV because one of the four Hf—O bonds is nearly broken. For neutral H^0, we also find that H is bonded to the threefold-coordinated O atom, similar to H^+, with the bond length of 0.981 Å. In this case, the formation of the O—H bond lowers the energy by about 1.0 eV, as compared to an interstitial position, while H^0 in SiO_2 favors an interstitial site without bonding to the host atom.[12] On the other hand, for a negative charge state, H^- is positioned at an interstitial site, as shown in Fig. 1(b), with the distance of 2.02 Å between the H and nearest Hf atoms, compared to the O—H bond distance of 2.14 Å to the nearest O atom. Since H incorporation into the Hf atom is accompanied by large lattice relaxations of the surrounding O atoms, the interstitial position is more preferable for H^-.

For H^0 and H^+, the antibonding state of the O—H bond lies above the conduction band minimum (CBM). Thus, H^0 behaves as a shallow donor, while H^- at the interstitial site has a deep localized state in the band gap. Figure 2(a) shows the formation energies of H^+, H^0, and H^- as a function of the Fermi energy (E_F). As the Fermi energy increases, the charge state changes directly from positive to negative, indicating the *negative-U* behavior,[13] similar to that found in various semiconductors and insulators.[14–16] From the $(+/0)$ and $(0/-)$ transition levels, we find a large negative value of $U=-1.6$ eV, which is mainly due to the highly ionic bonding nature of HfO_2. The $(\pm)$ transition level of H is located at about 2.9 eV above the valance band maximum (VBM), and this result agrees with the universal alignment rule for H transition levels.[17] Considering the conduction band offset of 1.5 eV between HfO_2 and Si and the maximum band bending effect of about 1 eV, the Fermi level in the MOS device structure is expected to be positioned above the hydrogen $(\pm)$ transition level. Then, the incorporated H will be in a negative charge state, with occupying the interstitial region. This result rules out the possibile formation of H-induced overcoordinated oxygen centers in HfO_2 gate dielectrics during the postannealing process.[2] We also investigate the energetics of an H_2 molecule in HfO_2, and find that H_2 at an interstitial site is more stable than H^- or H^+, for a narrow range of the Fermi levels between 2.5 and 3.2 eV, as shown in Fig. 2(a).

Next we discuss the role of oxygen vacancy on fixed charge defects. In monoclinic HfO_2, there occur two types of O vacancies, $V_O(3)$ and $V_O(4)$, which are surrounded by 3 and 4 Hf atoms, respectively, and both the O vacancies produce donor levels in the band gap. Figure 3(a) shows the contour plot of charge densities for the localized donor level of $V_O(3)$. It is evident that the defect state mainly consists of Hf *d* orbitals with relatively lower densities at the vacancy position. We find that O vacancies behave as a charge trap in HfO_2, consistent with previous calculations.[18] When an oxygen vacancy forms a $V_O(3)$–H complex with hydrogen, H is located almost at the vacancy center, as shown in Fig. 1(c). In this configuration, the H atom can be regarded as a substitutional, and there is no defect level in the band gap due to strong interactions between the H and neighboring Hf atoms.

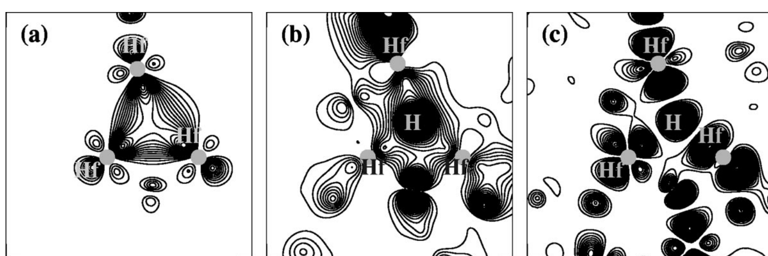

FIG. 3. Contour plots of the electron charge densities for (a) the defect state of V_O, and (b) the bonding and (c) antibonding states of the V_O–H complex.

Downloaded 19 Apr 2013 to 143.248.118.122. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://apl.aip.org/about/rights_and_permissions

Figures 3(b) and 3(c) show the charge densities for the bonding and antibonding states of the $V_O(3)-H$ complex. The bonding state of the $V_O(3)-H$ complex is located at 4.9 eV below the VBM, while the antibonding state lies above the CBM, indicating that this complex behaves as a shallow donor. From the formation energies in Fig. 2(b), we find that the $V_O(3)-H$ complex remains in a singly positive charged state, regardless of the position of the Fermi level. Since the defect level of the positive charged $V_O(3)-H$ complex is unoccupied, the relative stability of this complex is unaffected by the band gap error in the GGA calculations. To see the energetics of the $V_O(3)-H$ complex for different charge states, we examine the reactions of forming $[V_O(3)-H]^q$ $(q=1+,0,1-)$ from $V_O(3)^p$ and H^{q-p} and find them to be exothermic for all the combinations of p and q. For example, the binding energies are calculated to be 2.3 and 0.9 eV for the complexes of V_O^0 with H^+ and H^-, respectively. In Fig. 2(b), the formation energy of the $[V_O(3)-H]^{1+}$ complex is compared with those for well separated $V_O(3)^p$ and H^{q-p} in the most stable charge state. We find that the $[V_O(3)-H]^{1+}$ complex is energetically more stable against the dissociation into V_O and H for the Fermi levels above 1.4 eV, which covers the band gap of Si substrate. Recent experiments showed that the P_{b0} centers, which are likely to be formed near the Si/oxide interface, are depassivated possibly due to the release of H atoms during the postannealing process, while the density of positive fixed charge defects increases.[2] Considering the fact that the released H atom is likely to form the V_O–H complex, which appears to be the most stable defect among H-related complexes, we suggest that the positive charged V_O–H complex may be responsible for the increase of positive fixed charge defects by the postannealing.

Finally, we investigate the binding of OH in defect-free HfO_2, and find that the O atom is bonded to two Hf atoms, as shown in Fig. 1(d). The OH element is easily provided from H_2O, which is used as the oxygen source in growing HfO_2. Using the conjugate gradient method, we find that H_2O, which is initially located in the interstitial region, can be easily dissociated into OH and H, which are later bonded to the Hf and O atoms, respectively, with no energy barrier. After the dissociation of H_2O, the OH unit is found to remain in a negative charge state for the Fermi levels above 0.5 eV. This result indicates that the OH molecule may be a good candidate for defect centers giving the negative fixed charge in as-deposited samples.[2–5]

In conclusion, we find that although hydrogen in bulk HfO_2 is the *negative-U* defect, the defect complex of V_O and H is positively charged for all the Fermi levels in the band gap, donating an electron. The V_O–H complex is very stable against its decomposition into V_O and H, and this defect complex is suggested to be responsible for the formation of positive fixed charge defects, which neutralize negative fixed charges in the postannealing process of SiO_x/HfO_2 stack.

This work was supported by the MOST of Korea through the National Science and Technology Program (Grant No. M1-0213-04-0001) and by Samsung Electronics.

[1] A. I. Kingon, J.-P. Maria, and S. K. Streiffer, Nature (London) **406**, 1032 (2000).
[2] M. Houssa, V. V. Afanas'ev, A. Stesmans, and M. M. Heyns, Appl. Phys. Lett. **77**, 1885 (2000).
[3] S.-W. Nam, J.-H. Yoo, S. Nam, H.-J. Choi, D. Lee, D.-H. Ko, J. H. Moon, J.-H. Ku, and S. Choi, J. Non-Cryst. Solids **303**, 139 (2002).
[4] Y. Kim, G. Gebara, M. Freiler, J. Barnett, D. Riley, J. Chen, K. Torres, J. Lim, B. Foran, F. Shaapur, A. Agarwal, P. Lysaght, G. A. Brown, C. Young, S. Borthakur, H.-J. Li, B. Nguyen, P. Zeitzoff, G. Bersuker, D. Derro, R. Bergmann, R. W. Murto, A. Hou, H. R. Huff, E. Shero, C. Pomarede, M. Givens, M. Mazanec, and C. Werkhoven, Tech. Dig. - Int. Electron Devices Meet. **2001**, 20.21.
[5] S. J. Lee, C. H. Choi, A. Kamath, R. Clark, and D. L. Kwong, IEEE Electron Device Lett. **24**, 105 (2003).
[6] H. Iwai, S. Ohmi, S. Akama, C. Ohshima, A. Kikuchi, I. Kashiwagi, J. Taguchi, H. Yamamoto, J. Tonotani, Y. Kim, I. Ueda, A. Kuriyama, and Y. Yoshihara, Tech. Dig. - Int. Electron Devices Meet. **2002**, 26.4.1.
[7] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[8] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[9] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[10] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).
[11] J. Kang, E.-C. Lee, and K. J. Chang, Phys. Rev. B **68**, 054106 (2003).
[12] A. Yokozawa and Y. Miyamoto, Phys. Rev. B **55**, 13783 (1997).
[13] The GGA band gap of 3.6 eV is underestimated in HfO_2, as compared to the measured value of 5.7 eV. We note that the band gap error in the LDA does not affect the *negative-U* behavior of H; the defect state of H^+ is unoccupied, and for H^- at an interstitial site, the valence-band-like state will be little influenced.
[14] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).
[15] J. Neugebauer and C. G. Van de Walle, Phys. Rev. Lett. **75**, 4452 (1995).
[16] C. Kilic and A. Zunger, Appl. Phys. Lett. **81**, 73 (2002).
[17] Considering the electron affinity of 2.5 eV for HfO_2 [J. Robertson, J. Vac. Sci. Technol. B **18**, 1785 (2000)] and the GGA band gap error of 2.1 eV, it is expected that the hydrogen $(\pm)$ level lies at about 5 eV as an upper limit below the vacuum level, while previous calculations (Ref. 14) suggested the $(\pm)$ level of 4.5 ± 0.4 eV for various materials.
[18] A. S. Foster, F. Lopez Gejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B **65**, 174117 (2002).

Downloaded 19 Apr 2013 to 143.248.118.122. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://apl.aip.org/about/rights_and_permissions