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Sulfur passivation effect on HfO_2/GaAs interface: A first-principles study

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The impact of sulfur passivation on the structural and electronic properties of the HfO_2/GaAs interface is investigated by density functional theory with a hybrid functional. The gap states at the HfO_2/GaAs interface arise from three major contributions: Ga 3+ and partial oxidation, As–As dimers, and Ga dangling bonds. By introducing S atoms at the interface, the removal of the gap states within the lower half of the GaAs band gap is observed, while the gap states in the upper half are pushed upward by ~0.15 eV. © *2011 American Institute of Physics*. [doi:10.1063/1.3597219]

The existence of a high density of states in the band gap for metal-oxide-semiconductor (MOS) device interfaces remains a key impediment to achieve high speed microelectronic device performance.[1] In contrast to the well-established SiO_2/Si interface, achieving a low interface state density (D_{it}) for III-V MOS devices has encountered several obstacles. The major issue is the lack of an atomically and electronically abrupt interface, which attracts considerable research on investigating the origin of the interfacial gap states.[2–5] Using x-ray photoelectron spectroscopy (XPS), Hinkle *et al.*[6,7] showed that D_{it} is correlated with interfacial Ga 3+ oxidation states. This finding is consistent with the fact that when the interface is passivated by amorphous-Si, the Ga 3+ oxidation state is reduced at the interface and a significantly reduced D_{it} is observed.

To minimize the D_{it}, extensive work on the GaAs surface and interface passivation have been performed during the last decade.[6,8–11] A passivation treatment using sulfur during GaAs surface preparation was reported to improve electrical performance of III–V MOS devices fabricated by a subsequent atomic layer deposition of high-k dielectric.[12,13] Nevertheless, the bonding configuration at the sulfur-passivated interface is not fully revealed. Recently, Aguirre-Tostado *et al.*[14] observed that the GaAs surface treated by $(NH_4)_2S$ showed a decreased band bending, due to the reduction in interfacial space charge with respect to $(NH_4)OH$. This bending was attributed to a binding energy shift to higher energies for S-passivated surfaces. However, the need for a systematic fundamental knowledge of how S atomically changes the interface bonding and thus passivates the HfO_2/GaAs interface states remains. Our previous studies[15] assign the gap states to As–As dimers, Ga partial and 3+ like oxidation and Ga dangling bonds (db). In this letter, we further apply the Heyd–Scuseria–Ernerhof (HSE)[16] hybrid functional to obtain an accurate band gap and the locations of the gap states. Furthermore, we show the S passivation effect on the interface and provide an atomic level insight of gap state removal mechanism.[15]

Our calculations are based on the density functional theory with the generalized gradient approximation which was proposed by Perdew, Burke, and Ernzerhof (PBE),[17] as implemented in the plane-wave basis code VASP.[18] The pseudopotential is described by the projector-augmented-wave method.[19] An energy cutoff of 400 eV and a $6\times6\times1$ k-point mesh are used. The geometry optimization is terminated when the Hellman–Feynman force on each atom is smaller than 0.01 eV/Å.[16] Electronic structure calculations are performed using a class of hybrid density functional, in which a fraction α (15%) of PBE exchange is replaced with Hartree-Fock exchange.[20] In this work, a slab model with a ~0.3% planar strain at the HfO_2/GaAs interface is used (see Ref. 20 for more details to generate the interface model).

Figure 1(a) depicts the HfO_2/GaAs interface[20] (labeled as O9/Ga4 according to the numbers of interfacial O and Ga atoms) at which two As–As dimers and one Ga dangling bond (highlighted by a dashed circles) are formed. Interfacial Ga atoms bond to different numbers of O atoms, indicating various Ga oxidation states which may also result in Fermi level pinning. To study how S can passivate the resultant interfacial gap states, various S substitutions and interstitials (up to four S atoms at the interface with different configurations) are examined. Experimentally, Aguirre-Tostado *et al.*[14] showed that S bonding peak was below the XPS detection limit, indicating a low concentration of S at the interface was observed. Moreover, Chen *et al.*[8] observed Ga–S bonding at

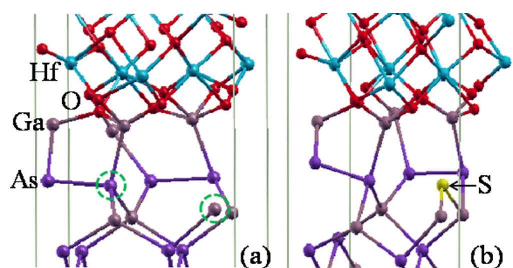

FIG. 1. (Color online) (a) and (b) represent side view of the GaAs:HfO_2 interface (O9/Ga4 and O9/S/Ga4 models). Ga, As, Hf, S, and O atoms are depicted by gray, purple, light blue, yellow, and red balls, respectively. The Ga atoms with dangling bonds and an As dimer atom are highlighted by green dashed circles.

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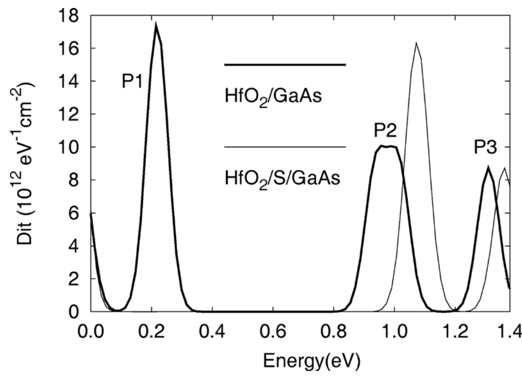

FIG. 2. Calculated interface state density D_{it} of interface HfO_2/GaAs and HfO_2/S/GaAs. VBM (CBM) is valence (conduction) band edge maxima (minima). P1, P2, and P3 are the D_{it} distributions within the GaAs band gap region without S passivation.

the HfO_2/GaAs interface from surface S treatments. Therefore, the best stability for the interface with one S interstitial is consistent with experiment, and we chose our model with one S interstitial located between the Ga and As, forming Ga–S and As–S bonds. Figure 1(b) shows the final relaxed configuration with only Ga–S bond formed without breaking As–As dimers, which agrees well with XPS observations.[14]

Figure 2 illustrates the D_{it} distribution with and without interfacial S atoms. The valence band edges of bulk GaAs are used as reference to line up these two D_{it} distributions. By performing the HSE correction, a bulk GaAs band gap of 1.40 eV was obtained, which agrees well with the experimental value 1.42 eV.[21] At the interface, three interfacial peaks labeled as P1, P2, and P3 are found. The partial charge density within the band gap states is plotted to explore the origin of these gap states. Figure 3(a) clearly shows that P1, P2, and P3 correspond to Ga partial oxidation (Ga3), As–As dimers and Ga (Ga5) dangling bonds, respectively. According to the Bader charge[22] calculation (in units of electron charge, e), Ga1, Ga2, Ga3, and Ga4 contain 1.64, 1.65, 2.19, and 1.55, respectively. Ga1, Ga2, and Ga4 oxidation states are close to the Ga charge of 1.30 e in bulk Ga_2O_3. However, Ga3 (bonded to three O and two As atoms) has 2.19 e which is neither close to that of Ga_2O_3 or GaAs, and this state corresponds to a partial oxidation state leading to gap states. The contribution of Ga1, Ga2, and Ga4 to the gap states are less than that of Ga3, which are not shown in Fig. 3(b) because a high electron density value was used to only visualize Ga3's contribution and avoid the difficulty to identify the partial charge distribution. As a result, we conclude that Ga 3+ and Ga partial charge states are responsible for the gap states P1.

With the presence of S at the interface, the Ga3 charge state is reduced from 2.19 e to 1.81 e while the Ga1 (bonded to three O and one As atoms) charge state is increased from 1.64 e to 1.69 e without changing the Ga–O bonding environment. The Ga dangling bond is removed by forming a Ga–S bond, but the associated Ga atom (with 2.23 e) is not fully saturated by S. Moreover, the As–As dimers survive after S is introduced into the interface. Consequently, states located in the lower half region of the gap are removed (P1 in Fig. 2), and two upper half trap peaks (P2 and P3) move upward slightly toward the conducting band. This partial passivation effect is also observed in experimental studies.[23] Therefore, the main effect of S passivation is to remove the P1 gap state near the valance band edge. Under the S passivation, newly formed Ga (Ga1) partial oxidation states and Ga–S bonding contribute to the gap states in the upper half region of the gap. As S cannot fully eliminate As–As dimers and recover Ga partial oxidized states, S has a limited passivation capability at HfO_2/GaAs interface.

For further device scaling potential with low gate leakage current, the dielectric layer is required to have sufficient barrier heights for both electron and hole tunneling which are determined by conducting band offsets and valence band offsets (VBO). The VBO is accurately predicted by the reference potential method.[24,25] For the interface O9/Ga4, the VBO is 1.81 eV compared to experimental values of 2.00,[26] 2.10,[27] and 2.85 eV.[28] The variation in experimentally determined VBOs indicates diversity among the samples analyzed, and the VBO difference between theoretical prediction and experimental measurement likely results from the variety of bond configurations due to the interfacial oxygen concentration. At the O9/S/Ga4 interface, we obtain a VBO of 1.98 eV. This finding confirms large enough tunneling barriers between HfO_2 and GaAs.

In conclusion, we used first principles methods with a hybrid functional to study the origin of gap states of at the HfO_2/GaAs interface and the S passivation effect on the interface. We find that Ga dangling bonds, Ga partial oxidation states (including Ga 3+ like) and As–As dimers contribute to the gap states. S passivation helps to remove the gap states within the lower half of the GaAs band gap and push the states in the upper half of the band gap upward toward the conducting band.

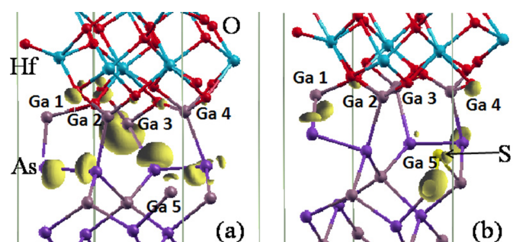

FIG. 3. (Color online) (a) and (b) represent the side view of the partial charge density of the interface O9/Ga4 and O9/S/Ga4 models. The Ga, As, Hf, S, and O atoms are depicted by gray, purple, light blue, yellow, and red balls, respectively. Light yellow color indicates partial charge distribution. The O9/Ga4 and O9/S/Ga4 model electron densities are 4×10^{-2} e Å^{-3} and 6.5×10^{-2} e Å^{-3}, respectively.

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