Intrinsic Origin of Negative Fixed Charge in Wet Oxidation for Silicon Carbide

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We demonstrate on the basis of first-principles calculations that the formation of carbonate-like moiety in SiO2 could be the intrinsic origin of negative fixed charge in SiC thermal oxidation. We find that two possible origins for the negative fixed charges are O-lone-pair state and a negatively charged CO3 ion in SiO2. Such CO3 ion is able to be formed as a result of the existence of residual C atoms in SiO2, which are expected to be emitted from the interface between SiC and SiO2, and the incorporation of H atoms during wet oxidation.

Silicon carbide (SiC) has recently attracted a great deal of attention as a promising material for the next generation of high-power and high-frequency electronic devices. One of advantages of SiC for practical application is the formation of insulating silicon oxide (SiO2) layers on SiC by thermal oxidation, being important for the fabrication of SiC-based metal-oxide-semiconductor field-effect transistors (MOSFETs). There are two types of oxidation processes; dry and wet oxidation. The dry oxidation process of SiC is performed in O2 atmosphere. On the other hand, the wet oxidation process is conducted in O2 and H2O atmosphere, and, as compared to the case of dry oxidation, the wet oxidation process is known to effectively reduce the deep donor-type interface states for the p-type MOS capacitors, leading to the improvement of the channel mobility of the MOSFET. Furthermore, wet oxidation yields high oxidation speed, twenty five times larger than that of dry oxidation, being also advantageous for realistic applications toward mass productions.

It is, however, serious issue encountered in wet oxidation. This treatment leads to surprisingly large amount of negative fixed charges near the SiC/SiO2 interfaces. The wet-oxidation-induced interface traps between SiC and thermal oxide SiO2 have been investigated experimentally by high-frequency C-V measurement of MOS capacitors. It has been reported that fixed charges near SiO2/SiC interfaces give large influences on threshold voltage and channel mobility of SiC-MOSFET. Notably, it has been pointed out that in wet oxidation the interface fixed charges increase up to \(-13\times10^{11}\) cm\(^{-2}\) (wet reoxidation annealed after wet oxidation) in p-4H-SiC MOS capacitor. Non-negligible negative fixed charge also appears during dry oxidation. Nevertheless, despite the extensive experimental outcomes, the origin of the negative fixed charge remains unclear for the last decade.

In this letter, we propose to clarify the atomistic origin of negative fixed charge appearing in SiC thermal oxidation processes on the basis of first-principles calculations in the framework of density functional theory (DFT). We here focus on residual C atoms in SiO2 which are expected to be emitted from the interface between SiC and SiO2. The existence of such residual C atoms is supported through a comparison with Si thermal oxidation. Indeed, it has been reported experimentally and theoretically that one-third Silicon atoms are inevitably emitted from the interface to release the stress induced during Silicon oxide growth.

Our calculations demonstrate that residual C atoms in SiO2 leads to the formation of carbonate-like ion assisted by incorporated H atoms. We find that the existence of the carbonate-like ion stabilizes 1- charge state, being the intrinsic origin of negative fixed charge in SiO2/SiC interface.

We considered three types of structural models based on 72-atoms α-quarts SiO2. The first model was constructed by substituting one C atom for Si, while the second and third models involve one and three H atoms, respectively. The lattice vectors were set to be \(a_1 = (1, -\sqrt{3}, 0)a, a_2 = (1, \sqrt{3}, 0)a, a_3 = (0, 0, 2)c\), where \(a = 4.944\) Å and \(c = 5.363\) Å, which was optimized for SiO2 bulk in the α-quarts phase. All calculations were performed using DFT with the Perdew-Burke-Ernzerhof generalized gradient approximation. We used ultrasoft pseudopotentials for Si, O and C and norm-conserving pseudopotentials for H. We used a plane-wave basis set with a cutoff energy of 36 Ry. We sampled 2×2×2 k-points in the Brillouin zone (BZ) for the BZ integration; using 3×3×3 k-points in the BZ gives a difference of 0.01 eV in total-energy for the system, assuring required accuracy in the present calculations. After the optimizations, all the atomic forces were less than 0.05 eV/Å. We used the background ion charge correction proposed by Blöchl to calculate the charged state.

Figure (a) shows the the formation energy diagram of the models including one C atom, one C atom and one H atom, and one C atom and three H atoms, respectively. We found that a defect with only C atom takes the neutral charge state for the whole range of the Fermi energy (the upper panel in Fig. (a)). However, the system including H atoms takes the 1− charge state for nearly the whole range of the Fermi energy (the upper panels in Fig. (b) and (c)). Particularly, if we assume that

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FIG. 1. (Color online) Formation energy diagram and optimized structures for the models including (a) one C atom, (b) one C atom and one H atom, and (c) one C atom and three H atoms in the unit cell. Dashed, solid, and dotted lines in the formation energy diagram show neutral, 1−, and 2− charge state, respectively. Optimized structures are shown for neutral state in the panel (a), and for 1− charge state for the panels (b) and (c). Distances are measured in units of Å.

the valence band offset parameter between 4H-SiC and SiO2 is 2.9 eV [19], the 1− charge state appears as the most stable state for all over the range of SiC band gap region. These results indicate that negative fixed charge is formed when both of C and H atoms exist.

Notably, we found that the structural origin of the stabilization for 1− charge state is the formation of carbonate-like ion. The lower panels in Fig. 1 shows the optimized structures for each model. It is clearly shown in the figure that carbonate-like (CO3-like) moiety is formed in SiO2 in the H-atom-included cases (Fig. 1(b) and (c)). The formation of CO3-like configuration is ascribed to H atoms that can cut Si−O bonds near the substitutional C atom, leading to the formation of strong sp2-like C-O bonds. These results provide clear indication that C atoms originating from SiO2/SiC interface leads to the formation of sp2 network in SiO2, which is assisted by H atoms.

There are two main factors for the stabilization of the CO3-like moiety. The first one is partial resonance in the CO3-like configuration. Indeed, as shown in the lower panels of Fig. 1(b) and (c), its C-O bonds are characterized as partially double bond and fully double bond, as compared with the typical lengths of the C-O single and double bonds (1.42 and 1.21 Å, respectively). The second factor is the formation of hydrogen-bonding between the CO3-like part and the nearby Si-O-H moiety (Fig. 1(c)).

The detailed structure of the CO3-like moiety depends on the number of incorporated H atoms in the system. In the case of the one H incorporation, two of three O atoms in the CO3-like part form covalent bonds with Si atoms (the lower panel in Fig. 1(b)). The CO3-like structure has C-O bonds of 1.26, 1.36, and 1.36 Å, and O-C-O angles of 113, 122, and 125 degrees. On the other hand, in the case of the incorporation of three H atoms, only one O atom in the CO3-like moiety form a covalent bond with Si atom (the lower panel in Fig. 1(c)). In this case, C-O bonds become 1.27, 1.29, and 1.36 Å, and O-C-O angles of 116, 121, and 123 degrees. These structural change of CO3-like moiety can be understood by considerations about its local bond network (Fig. 2). As compared with an isolated CO3-like ion, Si-O bond for-
Fig. 3. (Color online) Energy levels around energy gap at the Γ point and the distribution of wave functions for the system including one C atom and one H atom in 1− charge state. Energies are measured from the SiO$_2$ valence band top. The isovalues for the wave-function distribution are + 0.12 (gray) and − 0.12 (black) (e/Å$^3$)$^{1/2}$.

The incorporation of H atoms leads to a structural change of CO$_3$-like moiety, depending on the number of Si-O bonds. This chemical picture also strongly suggests that CO$_3$-like part is in 1− charge state when one Si-O bond is formed, while it is in neutral charge state when two Si-O bonds are created.

Indeed, a detail analysis of the electronic structure reveals that there are two origins for negative fixed charge, depending on the number of incorporated H atoms in the system. Figure 3 shows the energy level and the distribution of wave functions for the system including only one H atom in 1− charge state. There are five occupied gap states named α, β, γ, δ, and ε in the SiO$_2$ band gap region. The energy levels for the α, β, and γ states appear in the range of ~ 1 eV from the SiO$_2$ valence band top. These states are distributed primarily on CO$_3$-like moiety and the nearby O atom. On the other hands, the δ and ε states emerge above ~ 2 eV from the SiO$_2$ valence band top. These states are distributed only on O atom with lone-pair characteristics. These results indicate clearly that CO$_3$-like moiety is in neutral charge state, and an extra electron is trapped into O-atom lone-pair electron state, which leads to the intrinsic origin of negative fixed charge.

In sharp contrast, the three-H-atom incorporation case exhibits completely different electronic structure. There are only two gap states appearing above ~ 1 eV from the SiO$_2$ valence band top. The corresponding wave functions are distributed strongly in CO$_3$-like moiety. This indicates clearly that an extra electron is trapped into the CO$_3$-like part, and the moiety is in 1− charge state. The CO$_3$-like ion is thus the intrinsic origin of negative fixed charge when enough H atoms are incorporated in the system, and this could be possible in wet oxidation. In particular, the energy level for this defect state is deep as compared with SiO$_2$ large gap. This stabilization is ascribed to the formation of hydrogen-bonding between the CO$_3$-like ion and the nearby Si-O-H moiety as mentioned above. These results strongly suggest that the defect state originated from CO$_3$-like ion does not become a charge trapping level, but plays a strong negative-fixed-charge appearing in wet oxidation.

On the other hand, it has been experimentally reported that a few but non-negligible negative fixed charges appear during dry oxidation [9, 10]. In this case, the negative fixed charge could be O-lone-pair state. In reality, SiO$_2$ structure is amorphous. It is thus expected that a few O atoms which is not terminated by H can be formed near incorporated C atoms. This situation is similar to the case shown in Fig. 1 (b), where lone-pair electron state originated from non-terminated O-atom appears in SiO$_2$ band gap (Fig. 8).

Finally, we note charge-state-dependent behavior of H atoms near CO$_3$-like ion. As shown in Fig. 1 (c), a H atom terminates Si dangling bond when CO$_3$-like ion is formed. This H atom is, however, transferred from Si atom to one O atom in the CO$_3$-like ion when the system is in neutral charge state (Fig. 5), leading to the formation of Si dangling bond.
In conclusion, we have demonstrated that the formation of carbonate-like moiety in SiO$_2$ dielectrics could be the origin of negative fixed charges in the SiC thermal oxidation using first-principles calculations in the framework of DFT. Our calculations showed two possible atomistic origins for the negative fixed charges: O-lone-pair state and a negatively charged CO$_3$ ion. The CO$_3$ ion is able to be formed as a result of the existence of residual C atoms in SiO$_2$, which are expected to be emitted from the interface between SiC and SiO$_2$, and the incorporation of H atoms during wet oxidation.

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