Structural stability and energy levels of carbon-related defects in amorphous SiO₂ and its interface with SiC

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1. Introduction

Power electronics is one of fundamental technologies to realize our sustainable society. In this context, many researchers have paid attention to wide-gap semiconductors such as silicon carbide (SiC). The breakdown electric field of SiC is 10 times larger and its thermal conduction is 4 times larger than those of Si.1,2 Furthermore, as one of the good advantages, amorphous SiO₂ is easily formed on the SiC surface upon its thermal oxidation and utilized as an insulator in metal oxide semiconductor (MOS) devices. However, even in the commercially available SiC-MOS devices, high density of interface levels (Dit)3 and/or near interface traps (NIT) at the SiC/SiO₂ structure is a serious problem.4,5

To solve it, a lot of theoretical and experimental efforts have been done: Reported candidates for the Dit or NIT are carbon clusters,6–18 oxygen interstitials,19,20 stacking faults,21 silicon interstitials in SiO₂,22,23 SiC distortion induced by SiO₂,13,24 and intrinsic defects of SiO₂.25

In thermal oxidation of SiC, oxygen molecules or atoms diffuse in the SiO₂ film and react with Si atoms near the SiC/SiO₂ interface to form the SiO₂ bond network. During this process, C atoms near the SiC/SiO₂ interface are thought to be ejected as CO or CO₂ molecules and diffuse out eventually. However, substantial portion of the C atoms is expected to remain near the interface or in the SiO₂ films, presumably acting as Dit or NIT: In fact, Afanas’ev et al. discussed the existence of carbon clusters near the interface based on internal photoemission (IPE) spectroscopy;23 some other groups detected the carbon-related defects (C defects) near the interface using secondary-ion-mass spectrometry (SIMS) and discussed the relation between the C defects and electron mobility.26,27 From the theoretical side, density-functional calculations were done for SiC/SiO₂ interfaces and carbon-related defects (C-defects) are discussed.8,10,17,18

However, microscopic identification of C-defects in SiO₂ film has not been achieved yet. Works in the past have focused only on limited selections of C defects which are conjectured from empirical knowledge or educated guess, and then examined their properties. Systematic examination of the stability and the electronic structures of C defects is lacking. In this paper, we first prepare dozens of amorphous SiO₂ samples which contain carbon atoms by ab-initio molecular-dynamics simulations, then examine stability of various C defects based on the calculated formation energies, and clarify the energy levels induced by each C defect. We find that energetics of C defects is sensitive to chemical potentials of participating elements and thus the abundant forms of C defects depend on the position from the SiC/SiO₂ interface. We thus identify plausible C defects which are responsible for Dit and NIT.

2. Calculations

To explore abundant forms of C defects in amorphous SiO₂, we have performed melt-quench simulations based on Car–Parrinello molecular dynamics (CPMD)28 in which SiO₂ samples containing C atoms are heated to liquids and then are quenched to local minimum structures. The obtained 45 samples are representatives of the C defects in amorphous SiO₂. In the actual simulations, we use our real-space cutoff of 10,17,18 oxygen interstitials,19,20 stacking faults,21 silicon interstitials in SiO₂,22,23 SiC distortion induced by SiO₂,13,24 and intrinsic defects of SiO₂.25

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which the calculated SiO$_2$ gap is 8.7 eV. Orange area represents the SiC band-gap region. The band o

structural optimization has been done with a tolerance of the remaining forces less than $10^{-4}$ eV Å$^{-1}$. When we calculate electron energy levels, we have used a hybrid functional of Hyde–Scuseria–Ernzerhof (HSE06)\(^{41–43}\) in which Hartree–Fock mixing ratio of 0.5 and the screening parameter $\omega$ of 0.2 (au) are used to reproduce the band gap of SiO$_2$.

3. Results and discussion

3.1 Mono carbon defects

We start with mono-carbon defects. We prepare 25 samples which contain a single C atom and the different number of O atoms along with 26 SiO$_2$ units in a simulation cell, and performed the melt-quench simulations. The structure most frequently observed in the simulation is a CO molecule floating in a cavity of SiO$_2$ without making any chemical bonds with the SiO$_2$ network. We have then found eight different structures of the C defects bonding with the SiO$_2$ network, as shown in Fig. 1: The C atom takes three (defects labeled as #1, #2, #3, #4, #6, and #8) or four (defects labeled as #5 and #7) coordination number; a dangling O appears in the defects #1, #2, and #4.

The formation energy $F$ of the C-defect is defined as

$$F = E_d - E_0 - N_A\mu_A - N_C\mu_C - N_O\mu_O,$$

where $E_d (E_0)$ is the total energy of the simulation cell with (without) the C-defect, and $N_A$ and $\mu_A$ are the number of atoms in the simulation cell and the chemical potential of the element A. Considering the relations, $\mu_{Si} + 2\mu_O = E_{SiO_2}$ and $\mu_C + \mu_O = E_{CO}$ with $E_{SiO_2}$ and $E_{CO}$ being the total energies of SiO$_2$ and a CO molecule, respectively, the formation energy is expressed as a function of oxygen atom, e.g., $\mu_O$. The formation energy thus obtained is shown in Fig. 2. The range of $\mu_O$ in Fig. 2 includes the value for SiO$_2$ ($-9$ eV corresponding to the O-poor condition) and the value for an O$_2$ molecule ($-4$ eV; the O-rich condition). As a reference, we have also calculated the total energy of SiO$_2$ with a graphene sheet, modeling a situation where C atoms cluster in some forms.

In the O-rich region ($-6$ eV $\leq \mu_O \leq -4$ eV), we have found that the formation energy of the CO$_2$ molecule is the lowest and the C defect #7, where four O atoms surround the C atom, is the second lowest. The C defect #2 and the CO molecule follow. In contrast, in the O-poor region graphene in SiO$_2$ is the lowest, being indicative that C atoms tend to aggregate in the O-poor region. The C defects #8 and #5, where the C atom is surrounded by Si atoms alone, are relatively low in the formation energy. The C defect #4, in which the C atom is bonded with two Si and one O atoms, follows them. These defects thus are likely to exist under imperfect oxidation of SiC. In the realistic situation during the oxidation of SiC, $\mu_O$ is likely to have a position dependence along the direction perpendicular to the interface: Near the SiC/SiO$_2$ interface $\mu_O$ should be lower (O poor) compared with that far from the interface. Our results thus indicate that carbon clusters are easily formed (the defects #8, #5, and #4 may also be possible) near the interface. On the other hand, far from the interface, CO$_2$ molecules should be majority with the small amount of the defect #7 and #2.

Figure 3 shows calculated energy level ($q/q'$) at which the formation energies of the charge states $q$ and $q'$ are equal. It is of note that neither CO$_2$ nor CO induces the energy level in

![Fig. 1](image-url)  
**Fig. 1.** (Color online) Atomic structures of mono-carbon defects obtained by the melt-quench method. Red, blue, and brown balls depict the Si, O, and C atoms.

![Fig. 2](image-url)  
**Fig. 2.** (Color online) Formation energy of each mono-carbon defect shown in Fig. 1 as a function of oxygen chemical potential $\mu_O$. The formation energies of CO, CO$_2$, and graphene in SiO$_2$ are also shown.

![Fig. 3](image-url)  
**Fig. 3.** (Color online) Electron energy levels (charge transition levels) of each mono-carbon defect shown in Fig. 1 obtained by the HSE functional, in which the calculated SiO$_2$ gap is 8.7 eV. Orange area represents the SiC band-gap region. The band offset refers to the experimental value of Ref. 44.
the gap region of SiC. From the energetics viewpoint, the C defect #7 (O-rich) or #5 and #8 (O poor) are expected to be abundant, and #2 (O-rich) or #4 (O-poor) follows. We have found that the defects #4, #5, and #8 induce energy levels in the energy gap of SiC: The defect #5 induces an energy level ($-1/0$) near the conduction band bottom whereas the defect #4 and #8 do a deep level ($-1/0$). It is noteworthy that the defect #7 and #2 which are expected to exist in the O-rich region induces no levels in the gap. The defects #4, #5, and #8 which are expected to exist in the O-poor region are important near the SiO2=SiC interface. In particular, the defect #5 which induces a level near the conduction band is a strong candidate for the carrier trap.

### 3.2 Intrinsic defects in SiO2

We also discuss the intrinsic defects of SiO2. In the above samples generated by the melt-quench method, we have observed four intrinsic defects in amorphous SiO2 as shown in Fig. 4: Oxygen vacancy (labeled as #1), five-fold coordinated Si atom (labeled as #2), dangling Si=O bond (labeled as #3), and peroxide (labeled as #4). We have calculated the electronic energy levels of them in Fig. 5. All the defect structures cause several energy levels in the SiO2 energy gap. Especially, #2 and #3 defects induce deep levels in the gap of SiC.

### 3.3 Di carbon defects

We have then explored di-carbon defects by the melt-quench technique described above. We have prepared 20 amorphous SiO2 samples consisting of 24 SiO2 units with 2 carbon atoms. We have found that two carbon atoms are mostly relaxed to the mono-carbon structures that we have found above. In order to explore di-carbon structures, we use the blue moon method in which we impose a constraint that the distance between two carbon atoms is kept to be 1.3 Å. Consequently, we have found 12 distinct di-carbon-related defects in total, as shown in Fig. 6. The defect structures of the C atoms are categorized into two groups: line shape and ethylene-like shape: #1, #2, #8, #9, #10, and #11 are of the line shape structure, while #3, #4, #5, #6, #7, and #12 are of the ethylene-like structure. In the line-shape structures, one C atom is two-fold coordinated and the other C is three-fold (#1 and #2) or four-fold coordinated (#8, #9, #10, and #11).

Figure 7 shows calculated formation energies of these di-carbon defects. In the O-rich region ranging from $\mu_O = -7$ to $-4$ eV, we have found that the CO2 molecule is the lowest
in the formation energy even when we extend our search to di-carbon defects. We have also found that the second lowest is the CO molecule and that the formation energies of the di-carbon defects in this O-rich region is higher by several eV or more (Fig. 7). This fact means that in the O-rich region the existence of the di-carbon defects is unlikely. Since oxygen is relatively rich in the SiO2 region compared with the SiC cavity of SiO2 is most abundant and the mono-carbon rather than the di-carbon defect exists as a minority. In contrast, in the O-poor region which may be the region near the SiC/SiO2 interface, the generation of carbon clusters is the energetically favorable. However, interestingly the second lowest structures are the di-carbon defects in the order of #4, #5, and #1. In these di-carbon defects, C atoms are connected mainly with Si atoms. This feature is likely to appear under the imperfect oxidation and the present results clarify that this is energetically favorable. We have also performed ab-initio oxidation simulations considering SiC substrate explicitly and found the appearance of the di-carbon defects during the oxidation.\(^2\) The di-carbon formation is also reported in Refs. 13 and 47.

Figure 8 shows calculated energy level \((q/q')\) induced by the di-carbon defects. As stated above, neither CO nor CO\(_2\) in the cavity of SiO\(_2\) induces the energy level in the gap region of SiC. From the energetics viewpoint, the defects #4, #5, and #1 may be abundant in the O-poor region (near the interface) but the #5 and #1 does not induce the energy level in the gap. The defect #4, however, induces the energy level just below the SiC conduction-band bottom, being a candidate for the carrier trap.

4. Conclusion

On the basis of the density-functional theory, we have generated amorphous SiO\(_2\) and extensively explored stable structures of carbon-related defects using the melt-quench scheme, and then clarified the induced electron energy levels (charge transition levels) near the energy gap of SiC. The stability of the defects have been clarified in terms of the oxygen chemical potential which corresponds to the oxygen abundance near and far from the SiO\(_2\)/SiC interface.

In the region with the O-poor condition, i.e., near the SiO\(_2\)/SiC interface where the oxidation may be incomplete, it is found that carbon clustering is energetically favorable. In particular, a di-carbon defect in the form of Si\(_3\)-C\(_2\)-Si\(_3\) (the defect #4 in Fig. 6) is the most stable carbon-related defect and induces an energy level just below the conduction-band bottom of SiC, being a strong candidate for the electron trap. We have also found that a mono-carbon defect in the form of C–Si\(_4\) (defect #5 in Fig. 1) is energetically favorable and induces a trap level near the conduction-band bottom.

In the region with the O-rich condition, i.e., far from the SiO\(_2\)/SiC interface where the oxidation has been done enough, we have generally found that the most stable form of carbon is CO or CO\(_2\) in the cavity of SiO\(_2\). We have found that these forms induce no electronic levels in the gap region of SiC. We have also found two mono-carbon defects with relatively low formation energies. They have the shapes of the Si–O–CO–O–Si (the defect #2 in Fig. 2) or the C–O\(_4\) (the defect #7). We have found that these defects are electronically inactive.

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