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Passivation effects of fluorine and hydrogen at the $SiC-SiO_2$ interface

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High concentrations of defects at the $SiC-SiO_2$ interface significantly reduce the efficiency of the SiC-based microelectronics. Investigations of the defect passivation are thus of great importance. We report first-principles density-functional-theory calculations for the effects of fluorine and hydrogen in passivating the defects at the $SiC-SiO_2$ interface. The calculations show that the isolated point defects involving excessive carbon atoms can be passivated by atomic fluorine and hydrogen, separately or combined. The results further suggest that molecular fluorine may be more effective for the passivation of the interface defects than molecular hydrogen and hydrogen fluoride. © *2010 American Institute of Physics*. [doi:10.1063/1.3527943]

Current microelectronics based on silicon (Si) cannot operate directly at high-temperature and high-power environments. As a result, silicon carbide (SiC) has been considered as a replacement for applications in such environments.[1–3] SiC is a wide band gap semiconductor with high thermal conductivity, and it has stable native oxide, silicon dioxide (SiO_2), so that the $SiC-SiO_2$ interface is a suitable core part for the metal-oxide-semiconductor field-effect-transistors (MOSFETs).[1–4] However, the channel mobilities in SiC MOSFETs are significantly reduced by the high concentrations of defects at the interface, resulting in applications with low efficiency.[5–8] It is therefore important to passivate the interface defects in order to reduce the defect density to an acceptable level, preferably comparable to that of the $Si-SiO_2$ interface, for efficient applications.

Experimental attempts to passivate the $SiC-SiO_2$ interface have been made in recent years. Direct passivation by H_2 gas at moderate temperatures (~400 °C) shows no measurable effect while high-temperature (~1000 °C) H_2 annealing shows conflicting results.[5,9–11] However, atomic hydrogen shows some effect.[1] On the other hand, several groups have achieved partial passivation by nitrogen.[1,12–15] Furthermore, a combination of nitrogen and hydrogen shows a more significant effect.[1] Yet, the interface state density after the passivation by N and H is still very high. Further passivation of the interface defects is highly desired.

We employed first-principles density-functional-theory (DFT) calculations to study the effects of fluorine and hydrogen in passivating the defects due to the excessive carbon atoms at the $SiC-SiO_2$ interface formed during oxidation of the most widely used polytype for the SiC-based MOSFETs—4H–SiC. The calculations show that the defects caused by isolated single carbon atom and small correlated carbon clusters can be passivated by fluorine atoms, hydrogen atoms, or their combinations. The results also suggest that F_2 gas may be more efficient than H_2 gas in passivating the interface defects.

The DFT calculations were performed with the ultrasoft pseudopotentials and generalized gradient approximation exchange-correlation functionals.[16–19] Two periodically repeated supercell models were used to simulate the *ideal defect-free* $4H-SiC-SiO_2$ interface. The first model was generated based on the work of Devynck *et al.*[20] The supercell contains a (3×4) surface cell with four (0001) double-layers of 4H–SiC (with a Si-terminated surface) and an amorphous SiO_2. The amorphous part models the continuous random network locally, with the corner of one local structural unit shared with another (the Si–O–Si bond angles and the Si–O bondlengths vary). The density of the SiO_2 part, if the small portion right at the interface is not counted, is close to that of amorphous phase of SiO_2 material. In this model, the unphysical dangling bonds of the bottom C layer and the O atoms at the top of SiO_2 were saturated by H atoms. The supercell contains 85 Si, 48 C, 84 O, and 20 H atoms. The second model contains a (4×4) surface cell with three (0001) double-layers of 4H–SiC and a SiO_2 part, with 64 Si, 48 C, 36 O, and 16 H atoms.[21,1,22] The second one was used for comparison. Both models provided similar results, and we only report the results obtained with the first model. For structure optimizations, atoms of SiO_2 and the top four SiC layers were allowed to relax until the forces to the atoms were smaller than 0.05 eV/Å. We used the Γ point in the Brillouin zone for the relaxations, but the densities of states (DOS) were calculated with 10–15 inequivalent **k**-points. An energy cut-off of either 396 eV (when fluorine is not involved) or 425 eV (if fluorine is contained) was used in the calculations.

We investigated passivation of two kinds of interface defects that are caused by excessive carbon atoms produced during oxidation of SiC: (1) single C atom bonded in the oxide side of the interface and (2) correlated C atoms right at or near the interface. Various experimental measurements and theoretical investigations have demonstrated the existence of excess C atoms at the $SiC-SiO_2$ interface, and it is believed that the interface defects are primarily due to such carbon atoms.[1–3,5,21,23–26]

The most stable defect configuration due to a single C atom was previously identified to be a bonded structure in the SiO_2 network at or near the interface.[1,21,23] We confirmed this configuration [Fig. 1(a)]. The C atom is bonded to two silicon atoms and an oxygen atom. This defect has an occupied level in the band gap. Our calculations further show that, when a single H or F atom is bonded to the defect, the resulted configuration still has an occupied electronic level in

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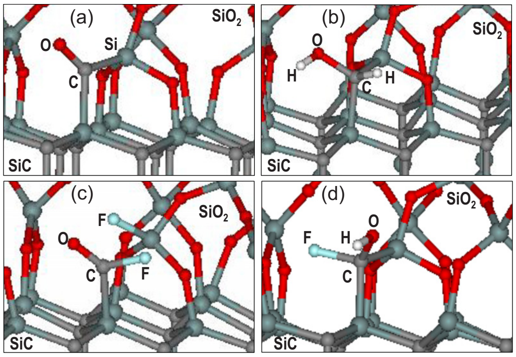

FIG. 1. (Color online) Schematics of the most stable configuration for the defect containing (a) a single C atom and (b) the corresponding local structures after two H atoms, (c) two F atoms, or (d) one H and one F atoms are bonded to the defect. The figures are viewed with slightly different orientations for better visualization.

the gap. Thus, a single H or F atom cannot passivate the defect.

However, when two H atoms react with the defect, one H atom is bonded to the O atom (bondlength: 0.98 Å), while the other is bonded to the C atom (bondlength: 1.1 Å) [Fig. 1(b)]. No states are found in the band gap. The defect state is thus removed by the two H atoms. Similarly, the defect state is removed by two fluorine atoms. Shown in Fig. 1(c), one of the two Si–C bonds is broken and the two F atoms are bonded to the Si and C atoms with bondlengths of 1.59 and 1.40 Å, respectively. When one H atom and one F atom are near the defect, in addition, the H atom is bonded to the O atom (bondlength: 0.99 Å) while the F atom is bonded to the C atom (bondlength: 1.46 Å) [Fig. 1(d)]. The defect state in the band gap is also eliminated. Thus, the isolated defect containing a single C atom can be passivated by two H atoms, two F atoms, or a combination of one H and one F atoms.

The second kind of the point defect is due to the correlated dangling bonds of excess C atoms (Fig. 2). Figure 2(a) shows a defect configuration *right at the interface*. This configuration was also previously identified.[1] The two central C atoms of the carbon cluster are threefold coordinated: one is bonded to three C atoms while the other is bonded to two C atoms and one O atom. Our DOS results shows that there are states in the upper part of the band gap (Fig. 3), and such defect states are due to the unsaturated C dangling bonds. We further identified another defect configuration. Shown in Fig. 2(b), it is also due to the correlated C dangling bonds of the two central C atoms, but the defect is located *in the SiC part of the interface* so that each of the two central C atoms is bonded to other three C atoms. We found that the defect states lie in the upper part of the band gap.

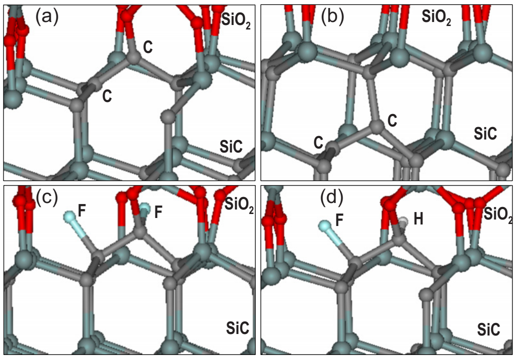

FIG. 2. (Color online) Schematics of the defects due to the correlated C dangling bonds (a) right at the interface or (b) near the interface and the resulted configurations after (c) two F atoms or (d) a combination of one H and one F atoms are bonded to the defect right at the interface.

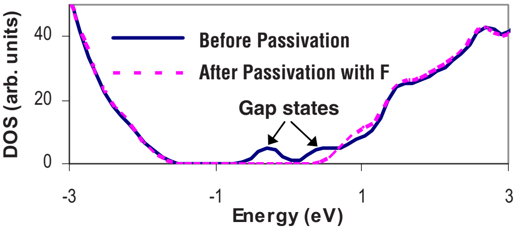

FIG. 3. (Color online) Total densities of states for the configurations due to correlated C dangling bonds before and after fluorine passivation [Figs. 2(a) and 2(c)]. Only the states in the vicinity of the band gap are shown.

Obviously, a single H or F atom cannot passivate the two correlated carbon dangling bonds. When two H atoms are bonded to the defects shown in Fig. 2(a) or Fig. 2(b), however, the C dangling bonds are all saturated. Each of the two H atoms is bonded to a correlated C atom. A similar result for the case of the defect right at the interface was previously reported.[1] As one would expect, there are no states in the band gap. Thus, the defect is passivated by two H atoms if they are bonded to the dangling C atoms. The binding energy of the two H atoms relative to the gas-phase molecule is calculated to be 2.2 eV, suggesting a stable bonding configuration. The diffusion barrier of H_2 molecule in amorphous SiO_2 was previously determined to be fairly small, ~0.4–0.5 eV, implying that H_2 can easily reach the interface.[27,28] As indicated in a previous study,[1] however, a large energy barrier may be involved in the dissociation of H_2 gas (in order to generate monoatomic H), accounting for the experimental observation that H_2 gas is not very effective for the passivation.[1,5,9,11]

On the other hand, our calculations show that fluorine may have a more effective passivation effect than hydrogen. Figure 2(c) shows the atomic structure of the defect after two F atoms are bonded to the two dangling C atoms located right at the interface. The F–C bondlengths are about 1.45 Å while the C–C bond between the two central carbon atoms has a bondlength of 1.50 Å. The geometry itself suggests that the two C dangling bonds are saturated by the F atoms, and the DOS result (Fig. 3) confirms that the defect states in the gap are indeed removed. The binding energy of two F atoms with the defect, relative to F_2 molecule, is 4.6 eV, indicating a strong bonding. Such strong F–C bonds replace the C dangling bonds upon the fluorine passivation, resulting in the shifts of the defect states out of the band gap. The same effect is also found for passivation of the defect in the SiC side near the interface shown in Fig. 2(b). Thus, two F atoms can passivate the defect caused by two correlated C atoms that are *right at or near the interface*. An important relevant fact is that the F_2 molecule has a much lower binding energy than the H_2 molecule, implying that the dissociation of F_2 gas would involve a significantly smaller barrier than that of H_2. Such a fact suggests that fluorine gas may be more effective than hydrogen gas for passivating the interface defects, especially for the correlated C dangling bonds right at and near the interface.

If one H atom and one F atom are bonded to the defect, similarly, the two correlated C atoms are saturated [Fig. 2(d)]. However, the HF molecule has an even higher binding energy that the H_2 molecule. Thus, the HF gas may not be effective for passivation. Note that it might not be possible to use fluorine for passivating the correlated C dangling bonds that are located in the *deep* SiC substrate because the F atoms would form other defect configurations before they could reach the dangling C atoms. Furthermore, fluorine gas is very active so that excess incorporation may not be efficient in reducing the defect density since fluorine could produce additional defects, particularly the defects in the SiO_2 network with five-coordinated Si which has, in addition to the usual four Si–O bonds, the fifth bond with a fluorine atom.

In conclusion, first-principles calculations show that hydrogen atoms, fluorine atoms, or their combinations can passivate, if they are bonded to the defects, the isolated point defects containing a single carbon atom or correlated carbon atoms at the $SiC-SiO_2$ interface. We suggest that the quality of the interface may be improved by incorporating F in the form of molecules, which could react with the interface defects and dissociate into atoms. While the passivation effects of fluorine have not yet been examined experimentally, we predict that F_2 may be more effective in passivating the defects than H_2 provided that the incorporation of fluorine is carefully controlled.

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