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APPLIED PHYSICS LETTERS **106**, 081601 (2015)

First-principles study on the effect of SiO_2 layers during oxidation of 4H-SiC

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The effect of SiO_2 layers during the thermal oxidation of a 4H-SiC(0001) substrate is examined by performing the first-principles total-energy calculations. Although it is expected that a CO molecule is the most preferable product during the oxidation, CO_2 molecules are mainly emitted from the SiC surface at the initial stage of the oxidation. As the oxidation proceeds, CO_2 emission becomes less favorable and CO molecules are emitted from the interface. We conclude that the interface stress due to the lattice constant mismatch between 4H-SiC(0001) and SiO_2 is responsible for the removal of C during the oxidation, resulting in the characteristic electronic property of the interface fabricated by the thermal oxidation. © *2015 AIP Publishing LLC*.
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Silicon carbide (SiC) has attracted considerable attention owing to its excellent physical properties, such as its high thermal conductivity, high breakdown strength, and large band gap. It is also advantageous that the oxidation of SiC leads to SiO_2, since it is well known that SiO_2 exhibits good dielectric properties in Si device technology. Therefore, the application of SiC in metal-oxide-semiconductor field-effect transistors (MOSFETs) has been studied with the aim of realizing high-temperature, high-power, and high-frequency electronic devices. Among the numerous polytypes of SiC, the 4H polytype has been recognized as the most promising material for applications because of its higher bulk mobility and larger band gap. However, unlike Si MOSFETs, SiC MOSFETs have unacceptably low carrier mobility. One of the origins of the low carrier mobility is the generation of a large number of interface defects at the SiC/SiO_2 interface during the thermal oxidation. Okamoto *et al.*[1] reported that the carrier mobility increases when the interface defect density is reduced. To increase the carrier mobility of SiC MOSFETs, understanding and precise control of the electronic structure of the SiC/SiO_2 interface are indispensable.

Since SiC consists of the same number of C atoms and Si atoms, both C emission and Si emission[2,3] during the oxidation process should be taken into account. The behavior of C atoms during oxidation is considered to play an important role, regardless of the interfacial atomic structure. The C emission process related to the SiC/SiO_2 interface has been studied by performing the first-principles calculations. Ventra and Pantelides[4,5] studied the atomic-scale mechanism of the growth of the SiO_2 region in cubic SiC bulk and concluded that a SiO_2 molecule unit and a CO molecule are generated when three O atoms are inserted in the cubic SiC bulk. Knaup *et al.*[6] and Deák *et al.*[7] investigated the CO emission process by following the dry oxidation process of SiC using a 4H-SiC(0001)/SiO_2 interface model. It is claimed that the reaction causing CO emission competes with that causing C cluster generation such as C or C_2 interstitials. It is believed that CO molecules are dominantly emitted from the interface during the oxidation; although a CO_2 molecule is the most stable product among the carbon oxides. However, there are no theoretical studies comparing the formation energies between the CO and CO_2 emissions at an advancing 4H-SiC/SiO_2 interface because direct calculations of the atomic-scale processes that occur at the interface are computationally demanding. In particular, calculation of the formation energy of interface defects generated by oxidation requires a large supercell in the lateral direction.

In this study, first-principles calculations are carried out to examine the effect of SiO_2 layers on the C removal process during the oxidation of a 4H-SiC(0001) substrate. The most stable sites for each O atom inserted into a Si-C bond are calculated by sequentially inserting O atoms between Si-C bonds to investigate the oxidation process of SiC. It is found that the second O atoms enter the Si-C bonds inside the substrate before the Si-C bonds in the upper layer are oxidized so as to suppress the increase in the lattice constant mismatch between 4H-SiC(0001) and SiO_2. Then, the energy gains of CO and CO_2 emissions are computed for each model by removing C and O atoms in the form of CO and CO_2 molecules, respectively. Interestingly, CO_2 emission preferentially occurs at the initial stage of the oxidation while CO emission becomes dominant as the oxidation proceeds. It is concluded that the interface stress due to the lattice constant mismatch plays an important role in the removal of C. The SiO_2 layers above the SiC substrate significantly affects the formation process of the interfaces during the thermal oxidation, which is relevant to the characteristic electronic property of the interface fabricated by the thermal oxidation.[8]

The first-principles calculations are performed within the framework of density functional theory[9] using the real-space finite-difference approach,[10–14] which provides us with the ground-state atomic and electronic structures using a time-saving double-grid technique.[12–15] In addition, the real-space finite-difference method enables us to execute the large-scale calculation using massively parallel computers,

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thus this method is suitable for the total energy calculations including interface defects. The electron-ion interactions are treated using the projector augmented-wave method[16] for the C, O, and Si atoms and using the norm-conserving pseudopotential[17] of Troullier and Martins[18,19] for H atoms. The exchange-correlation functional is approximated by the local density approximation.[20] The coarse grid spacing of 0.16 Å is used for all the calculations. Hereafter, the models for the initial and middle stages of the oxidation are referred to as the surface and interface models, respectively. For the calculation of the oxidation, the lateral size of the supercell is the $(6 \times 6\sqrt{3})$ 4H-SiC(0001) surface, and the substrate contains five (four) Si-C bilayers in the surface (interface) model. Dangling bonds at the bottommost Si-C bilayer as well as those at the topmost layers of SiO_2 are simply terminated by H atoms. The atomic structure of the initial surface for the thermal oxidation depends on the preparation of substrates. Since the studies exploring the epitaxial growth of a graphene on SiC surface report that bare SiC(0001) surfaces appear above 1000 °C in vacuum,[21] the bare surface is one of the realistic surface model. Thus, we chose the bare surface model for the initial oxidation. In the case of the interface model, although SiO_2 forms an amorphous phase after the oxidation of SiC, we assume that a crystalline structure remains locally near the SiC/SiO_2 interface, similarly to the Si/SiO_2 interface.[22] Therefore, interfaces consisting of α-quartz, α-cristobalite, β-cristobalite, and β-tridymite SiO_2 are considered. It is found that the 4H-SiC(0001)/β-tridymite SiO_2(001) interface has the smallest lattice constant mismatch among the interfaces. In addition, the ratio of the conduction band offset to valence band offset of the 4H-SiC/β-tridymite SiO_2 interface is in good agreement with that obtained by X-ray photoelectron spectroscopy. The details of the determination of the interface atomic structures will be reported elsewhere. In the interface model, the oxide region contains 60 SiO_2 molecule units, i.e., the thickness of SiO_2 is ~15 Å. Thus, the computational model for the surface before the insertion of O atoms includes 264 atoms and that for the interface contains 400 atoms. The periodic boundary condition is applied in all directions and a sufficiently thick vacuum region of ~14 Å is inserted. Only the Γ point is sampled in the Brillouin zone. We implement structural optimization until all the force components decrease to below 0.05 eV/Å. The atomic coordinates of the Si-C bilayer in the bottommost layer and the H atoms terminating C dangling bonds are fixed during the structural optimization.

We first calculate the oxidation energies by sequentially inserting O atoms into Si-C bonds around a particular C atom at the 4H-SiC(0001) surface, assuming the initial stage of the oxidation. Figure 1 shows the computational model after the structural optimization. It has been theoretically proved that O_2 molecules are the main species diffusing in the oxide during the oxidation.[23] It has also been reported that an O_2 molecule is not stable in SiC because of its relatively small interstitial volume and that it breaks into Si-C bonds so as to form Si-O-C bonds.[4] The oxidation energy for the insertion of an O atom into a Si-C bond at the surface, E_n^{ox}, is obtained from the expression

$$E_n^{ox} = E_{(n-1)O} + \mu_O - E_{nO}, \tag{1}$$

where n is the number of inserted O atoms, E_{nO} is the total energy of the system with n O atoms, and μ_O is the chemical potential of an O atom calculated from the total energy of an O_2 molecule. These values are determined by the density functional theory calculations at zero Kelvin.

Figure 2 shows the oxidation energy of the SiC surface for different values of n (white bars). According to Eq. (1), the oxidation is preferable when the formation energy is positive. It is found that the oxidation energies of the SiC surface are smaller than those at the Si(001) surface (3.0–5.0 eV).[2] The first O atom prefers the site between the Si-C bond in the first Si-C bilayer. On the other hand, the most preferential site of the second O atom is the Si-C bond between the first and second Si-C bilayers so that the increase in the volume in the direction parallel to the surface is suppressed. In the case of $n = 2$, the activation energy for the O_2 molecule to the ground state configuration from the metastable configuration, where an O atom is in the Si-C bond of the first bilayer and which is energetically high by 0.22 eV, is ~1.5 eV. By considering an activation energy of about 1.2 eV for the O_2 molecule transport in silica measured by the thermal oxidation of Si substrates,[24] some O atoms are stacked at the metastable configuration. The third O atom is preferentially inserted into the Si-C bond in the first Si-C bilayer again. We could not find the configuration in which three O atoms are inserted into the Si-C bonds in the first Si-C bilayer in the case of $n = 3$.

To investigate the C removal process, we remove a C atom in the form of a CO or CO_2 molecule from each model. Various possible sets of C and O atoms are removed from the oxidized surface and the most stable configuration is

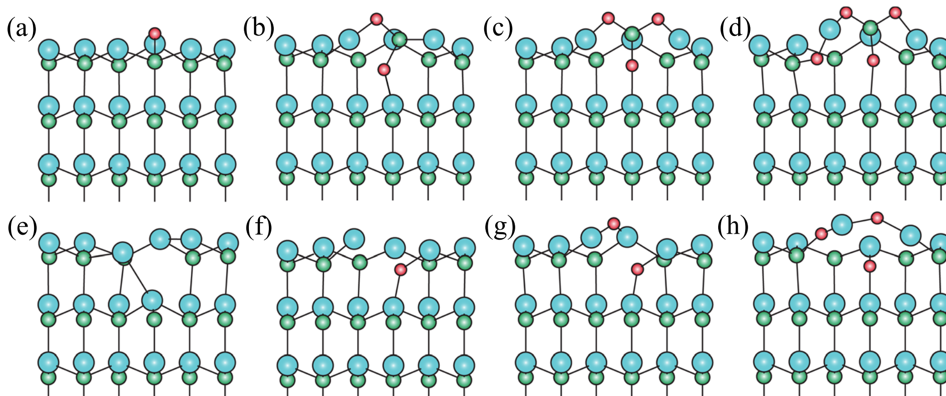

FIG. 1. 4H-SiC(0001) surface models with (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, and (d) $n = 4$ before C removal. (e), (f), (g), and (h) Surface atomic structures after CO emission from (a), (b), (c), and (d), respectively. The models are the structures after the structural optimization. Green, red, and blue circles are C, O, and Si atoms, respectively.

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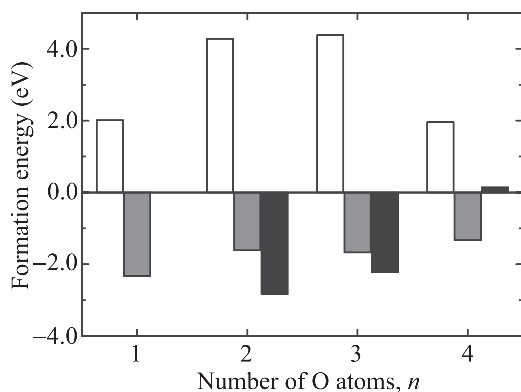

FIG. 2. Oxidation energies (white bars) and formation energies of CO emission (gray bars) and CO_2 emission (black bars) at SiC surface for different numbers of inserted O atoms, n.

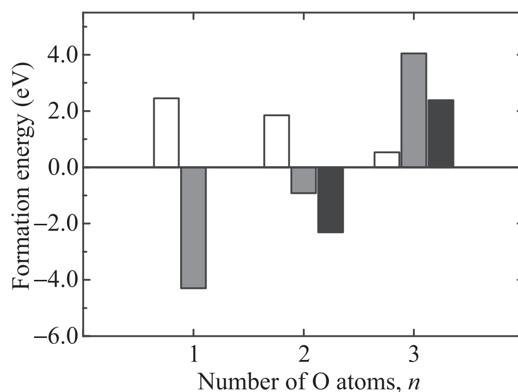

FIG. 4. Oxidation energies (white bars) and formation energies of CO emission (gray bars) and CO_2 emission (black bars) at SiC/SiO_2 interface for different numbers of inserted O atoms, n.

obtained. The energy gain of the emission from the system with n O atoms, $E_n^{CO_x}$, is given by

$$E_n^{CO_x} = E_{nO}^{w/C} - \left(E_{(n-x)O}^{w/o\,C} + \mu_{CO_x}\right), \tag{2}$$

where $E_{nO}^{w/C}$, $E_{(n-x)O}^{w/o\,C}$, and μ_{CO_x} are the total energy of the system with n O atoms, that with $(n-x)$ O atoms with one C atom missing, and the total energy of a CO_x molecule, respectively. The calculated energies of the CO and CO_2 emissions for different n are shown in Fig. 2 by gray and black bars, respectively. Positive (negative) formation energy indicates that the CO_x emission is preferred (not preferred). Interestingly, a CO_2 molecule is the most preferential species at the initial stage of oxidation contrary to the assumption employed in the experiments.[25] It is also found that CO emission is not favorable, although a perfect SiO_2 network is retained after CO emission in the case of $n = 3$ (see Fig. 1(g)).

To further investigate the oxidation process of SiC, we examine the emission of C from the 4H-SiC(0001)/SiO_2 interface at the middle stage of the oxidation as shown in Fig. 3. Figures 3(b)–3(d) show the optimized atomic structures of the interface during the oxidation. The preferential sites for the inserted O atoms are the same to those of the surface oxidation: the second O atom is preferentially inserted at the site in the Si-C bond connecting the first and second Si-C bilayers, while the first and third O atoms prefer the site in the first bilayer. In addition, the situation concerning the energy difference between the configurations and activation energy is similar to that of the surface oxidation. The calculated oxidation energies of the SiC/SiO_2 interface defined by Eq. (1) are shown in Fig. 4. Since the oxidation energies at the interface are smaller than those at the surface, it is slightly more difficult for the oxidation to proceed at the interface. This is because the SiO_2 on the SiC substrate prevents the interfacial atomic structure from relaxing.

Finally, we study the emission of C from the interface. The energy gains due to CO and CO_2 emissions are shown in Fig. 4. CO emission preferentially occurs at $n = 3$ because of the absence of Si dangling bonds and Si-O-C bonds after the emission (see Fig. 3(g)). On the other hand, CO_2 is not the most preferential emission species because the oxidation energy of Si is much larger than that of C; inserted O atoms are preferentially consumed to form SiO_2 units.

The CO emission at $n = 3$ and the CO_2 emission at $n = 4$ generate a perfect SiO_2 network containing neither dangling bonds nor Si-O-C bonds. It is intuitive that the insertion of O atoms increases the volume, which causes the deformation

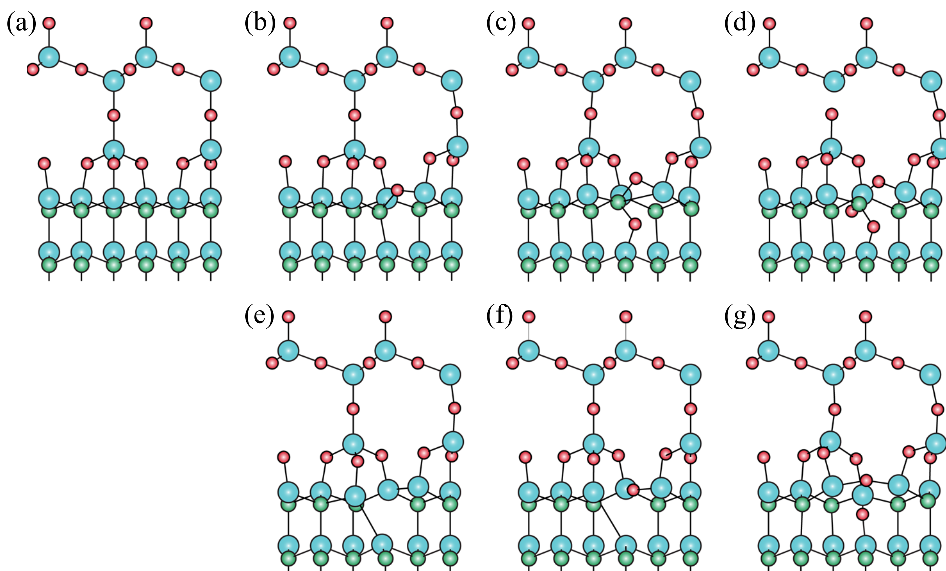

FIG. 3. 4H-SiC(0001)/β-tridymite SiO_2 (010) interface model. (a) Before insertion of oxygen, (b) $n = 1$, (c) $n = 2$, and (d) $n = 3$. (e), (f), and (g) Interface atomic structures after CO emission from (b), (c), and (d), respectively. The models are the structures after the structural optimization. The symbols have the same meaning as in Fig. 1.

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of the lattice. In the oxidation of the surface, the deformation of the lattice can be released owing to the absence of SiO_2, resulting in the negative energy gain of CO emission. On the other hand, in the oxidation of the interface, the presence of SiO_2 prevents the deformation of the lattice. Therefore, CO molecules are easily emitted from the interface so as to suppress the expansion of the SiC substrate when three O atoms are inserted.

Our results indicate that the formation of the interfaces is affected by the interface stress due to the lattice constant mismatch between 4H-SiC(0001) and SiO_2. It is known that the electronic structure of the interface fabricated by the thermal oxidation shows different characteristics from that formed by the oxide deposition.[8] The interface stress causes this difference in the electronic structure during the thermal oxidation.

In summary, we have conducted a systematic study of the C removal process during the oxidation of a 4H-SiC(0001) substrate by first-principles calculations. It is revealed that the oxidation energy of SiC(0001) is smaller than that of Si(001). The most stable site for the second inserted O atom is at the middle of the Si-C bond connecting the first and second Si-C bilayers for both the SiC(0001) surface and the SiC(0001)/SiO_2 interface. More interestingly, by calculating the total energy of an advancing 4H-SiC/SiO_2 interface, we found that CO_2 molecules are the most preferential species at the initial stage of oxidation, which is different from the conventional expectation. As the SiO_2 layer grows, CO emission becomes favorable. By examining the atomic structures before and after the emissions, we conclude that the presence of SiO_2 above the SiC substrate plays an important role in determining the emission species as well as in relaxing the bonding networks at the oxidation front, which gives rise to the difference in the electronic structures between the interfaces fabricated by the thermal oxidation and oxide deposition.

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