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Density Functional Theory Study for Adsorption of Oxygen and Water Molecules on 6H-SiC(0001) Surface

Chun-he Fu[a], Hui-li Lu[b], Shao-rui Sun[b*]

a. The 45th Research Institute of China Electronics Technology Group Corporation, Beijing 100176, China
b. Beijing Key Laboratory for Green Catalysis and Separation, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

6H-SiC is an important semiconductor material. The 6H-SiC wafer is always exposed to a high-humidity environment and the effect from the absorbed water molecule and some relative adsorbates is not negligible. Here, the oxygen and water molecules absorbed on the 6H-SiC(0001) surface and the dissociation process were studied with density functional theory. On the 6H-SiC(0001) surface, absorbed O_2 is spontaneously dissociated into O^*, which is absorbed on a hollow site, and further transforms the 6H-SiC(0001) surface into SiO_2. The absorbed H_2O is spontaneously broken into OH^* and H^*, which are both absorbed on the top of the Si atom, and OH^* is further reversibly transformed into O^* and H^*. The H^* could saturate the dangling Si bond and change the absorption type of O^*, which could stabilize the 6H-SiC(0001) surface and prevent it from transforming into SiO_2.

Key words: 6H-SiC(0001) surface, H_2O absorption, Dangling Si bond, Stability, Density functional theory

I. INTRODUCTION

Silicon carbide (SiC) is an important semiconductor material that has outstanding inherent advantages, such as excellent chemical stability, a high melting point, high hardness, high stiffness, large thermal conductivity, a large band gap and a high saturation value of electron drift, and it can be used in high-power, high-temperature, and high-frequency devices [1, 2].

SiC has many different polytypes, such as 3C-SiC (cubic), 2H-SiC (hexagonal), 4H-SiC (hexagonal), and 6H-SiC (hexagonal), and the band gaps differ widely among the polytypes: 2.3 eV for 3C-SiC, 3.3 eV for 2H-SiC, 3.2 eV for 4H-SiC, and 3 eV for 6H-SiC [3]. Different SiC polytypes could be applied to construct special MOSFET and high-voltage diodes [4, 5].

Of the polytypes, 6H-SiC is the most easily prepared and best studied. To obtain a high-quality electronic device, it is important to ensure that 6H-SiC has a clean and undamaged surface. Some absorption processes, especially for the oxygen molecule, have been extensively studied, and the top layer of the SiC surface could be transformed into SiO_2 under ambient conditions with a high O_2 concentration [6−16]. The 6H-SiC wafer is cut along the (0001) surface. During the cutting process,

water is used to cool the temperature, which implies that the surface is exposed in the ambient condition to a high water vapor concentration. In some studies, SiCs were reported to be as catalysts for the water splitting reaction and hydrogen evolution reaction (HER), which indicates that there are strong interactions between the SiC surface and water molecule or hydrogen atom [17, 18]. Then, on the 6H-SiC(0001) surface, the absorbed water molecule and some relative adsorbates should not be negligible.

Tsuchida et al. studied the Si−H bonds on the 6H-SiC(0001) surface after H_2 annealing and suggested that the surface was primarily terminated by silicon monohydride with high regularity [19]. Newsome et al. simulated the oxidation process of SiC by O_2 and H_2O under high temperature with a molecular dynamics method and found that SiC gradually transforms into the oxides of silicon with the simultaneous formation of a graphite-like layer under these high temperature [20]. Li et al. explored the hydrogen generation and water splitting on Si-terminated 4H-SiC(0001) surfaces. Until now, no work was reported to comprehensively study the behavior of the absorbed water molecule on the 6H-SiC(0001) surface [21].

In this work, the oxygen and water molecules absorbed on the 6H-SiC(0001) surface and their dissociation process have been studied with density functional theory (DFT). The calculation results show that H_2O could be spontaneously dissociated into absorbed OH^* and H^* and that the absorbed H^* could stabilize the

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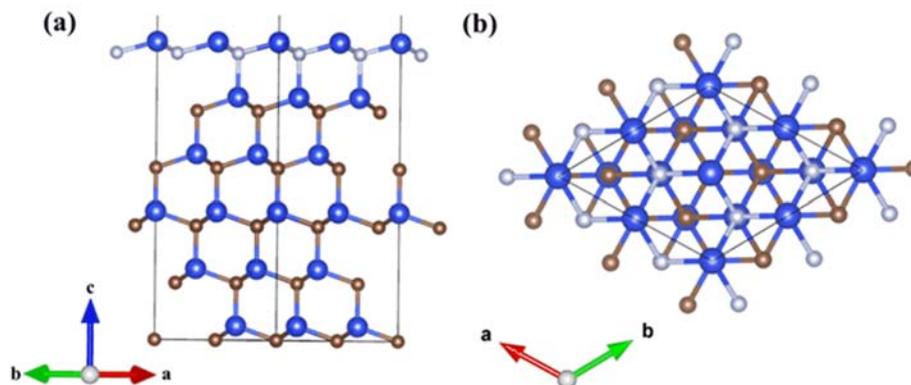*Author to whom correspondence should be addressed. E-mail: sunsr@bjut.edu.cn

FIG. 1 (a) The side view of the 6H-SiC(0001) surface and (b) the bird's-eye view of the surface, in which the blue ball is for the silicon atom, the brown for the carbon atom (h_2 site), and the gray for the carbon atom in the top layer (h_1 site).

6H-SiC(0001) surface. In the atmosphere with high humidity, the structural stability of the 6H-SiC(0001) surface could be improved.

II. CALCULATION METHOD

The DFT calculations in the present work were performed using the Viena *ab initio* simulation package (VASP) code [22]. The ion-electron interaction was processed with the projected augmented wave (PAW) approach [23, 24]. The PBE function (Parameterized by Perdew, Burke and Ernzerhof) [25] was used to evaluate the exchange-correlation energy. For the bulk calculation of platinum, $5 \times 5 \times 5$ k-point sampling was set in the first Brillouin zone. For the surface calculation, $5 \times 5 \times 1$ k-point sampling was used. The spin polarization was considered in the calculation. The Methfessel-Paxon method was used to determine the electron occupancies with a smearing width of 0.1 eV. The energy cutoff was set at 400 eV. The convergence criteria for the electronic self-consistent iteration and the ionic relaxation loop were set to 10^{-5} eV and 10^{-4} eV/Å, respectively. The 6H-SiC(0001) surface were constructed with 6-layer slabs, in which the top three layers were completely relaxed, and the 2×2 surface unit cell was set. The width of the vacuum space between two slabs was approximately 17 Å.

The absorption energy is calculated with the following equation:

$$E_{ab} = E_{surf\text{-}M} - E_{surf} - E_M \qquad (1)$$

where E_{ab} is the absorption energy, E_{surf} is the total energy of the surface, E_M is the total energy of the molecule, and $E_{surf\text{-}M}$ is the total energy of the surface and molecule after absorption.

III. RESULTS AND DISCUSSION

In the 6H-SiC(0001) surface, the silicon atom is at the terminal, as shown in FIG. 1(a), and compared with

the distance between the (000-1) crystal plane in the body phase, the distance between the two top layers is contracted by approximately 4%. Through the bird view, the carbon and silicon atoms in the top layer do not change their positions in the ab plane (as shown in FIG. 1(b)), and the Si−C bond length decreases slightly by approximately 2%, which is due to the structural contraction in the c direction.

On the 6H-SiC(0001) surface, there are two different hollow sites: the first is specified as h_1, which is just above the carbon atom of the top layer (the gray ball in FIG. 1(b)), and the second is h_2, which is just above the carbon atom in the second layer (the brown ball in FIG. 1(b)). For the oxygen molecular absorption, three end-on types are considered: on the top of the silicon atom (noted as the Si-end), on the h_1 hollow site (noted as the h_1-end), and on the h_2 hollow site (noted as the h_2-end). On the Si and h_1 sites, the side-on absorption types are both considered, which are noted as the Si-side and h_1-side, respectively. Three bridge-type absorptions are calculated in this work: the first is between two neighboring silicon atoms (noted as Si-Si), the second is between a silicon atom and its neighboring h_1 site (Si-h_1), and the third is between two neighboring h_1 sites (h_1-h_1). After complete optimization, all of the side-on and bridge absorption types are automatically dissociated, and the O=O double bonds are completely broken.

Table I shows the absorption energy of the oxygen molecule at different sites, although none of the three end-on types are dissociated (on the top of silicon atom, as shown in FIG. 2(a)), their absorption energies are obviously smaller than those of the dissociated types, which means the end-on types could not exist. After dissociation, the oxygen atom could be on the h_1 site, the h_2 site (FIG. 2 (b)), and the top of the silicon atom (FIG. 2(c)), in which the absorption energy on the h_2 site is the largest. It demonstrates that the dissociated oxygen on the h_2 site is energetically favorable. Then after the oxygen molecule is absorbed on the 6H-SiC (0001) surface, the O=O bond is completely broken

TABLE I The absorption energy of the oxygen molecule.

Absorption type before optimization		O=O bond length/Å	O* position after optimization	Absorption energy/eV
End-on	Si-end	1.37	–	−4.50
	h_1-end	1.30	–	−4.23
	h_2-end	1.33	–	−4.14
Side-on	Si-side	Dissociated	Top of the Si atom	−6.28
	h_1-side	Dissociated	h_2 site	−10.43
	h_2-side	Dissociated	h_1 site	−2.81
Bridge	Si-Si	Dissociated	h_2 site	−10.43
	Si-h_1	Dissociated	h_2 site	−10.43
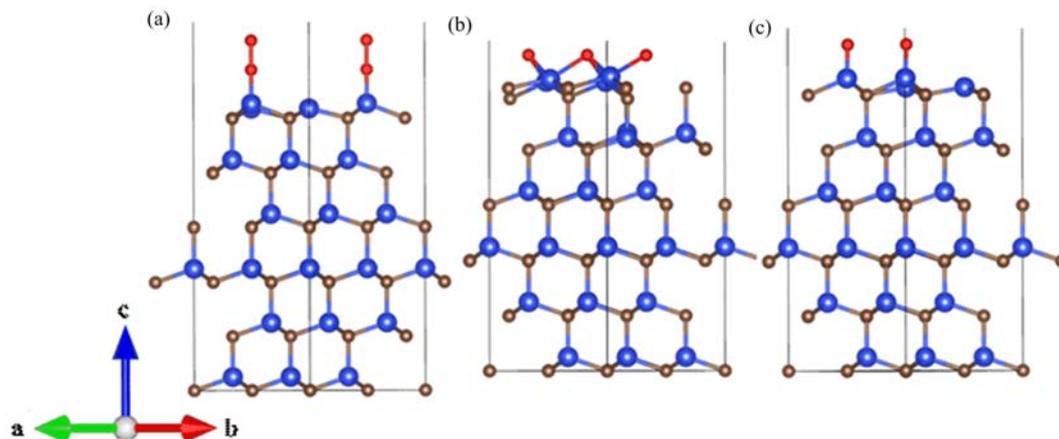
FIG. 2 (a) The oxygen molecule absorbed on the top of the Si atom, (b) the oxygen atoms after dissociation and absorbed on the h_2 site, and (c) the oxygen atoms absorbed on the top of the Si atom.

and the two dissociated oxygen atoms are absorbed on h_2 sites. The dissociated process is spontaneous and exothermic process without any energy barrier.

To confirm the above calculation results, the absorption of a single oxygen atom is evaluated. Three absorbed sites, *i.e.*, the top of the Si atom, the h_1 site, and the h_2 site, are considered. According to the calculation results shown in Table II, the oxygen atom is energetically favorable for absorption at the h_2 site.

For the hydrogen atom, the absorption on the three sites, the top of the silicon atom, the h_1 site, and the h_2 site are also evaluated. As shown in Table II, the hydrogen atom absorbed on the silicon atom is energetically favorable.

For a water molecule absorbed on the 6H-SiC (0001) surface, three different types are considered. The first is a water molecule absorbed on the top of the Si atom, the second is a molecule on the h_1 site and the third is a molecule on h_2 site. After complete geometry optimization, the water molecules on the three sites could not be stable and are all automatically dissociated into hydroxyl (OH*) and hydrogen atoms (H*), which are absorbed on the neighboring silicon atoms, as shown in FIG. 3(a). Similar to the oxygen molecule absorbed on the surface, the dissociation of the water molecule

is also a spontaneous and exothermic process without energy barrier.

The hydroxyl (OH) group is associated with absorption on the silicon atom, the h_1 site, and the h_2 site, and after geometric relaxation, the three absorption types are all optimized into the same final structure, and the group is absorbed on the top of the silicon atom. The absorbed hydroxyl (OH) group may be further dissociated into oxygen and hydrogen atoms (FIG. 3(b)) as in the following reaction:

$$OH^* \rightarrow O^* + H^* \qquad (2)$$

where OH*, O*, and H* are the absorbed hydroxyl (OH) group, oxygen, and hydrogen atom, respectively. The energy difference (ΔE) of the reaction is approximately 0.01 eV, which is a small value and implies that the reaction process is reversible. When the absorbed hydrogen atom is a neighbor of the oxygen atom, the oxygen atom is not on the h_2 site but on the top of the silicon atom.

The absorbed hydrogen atom can occasionally be transformed into a hydrogen molecule:
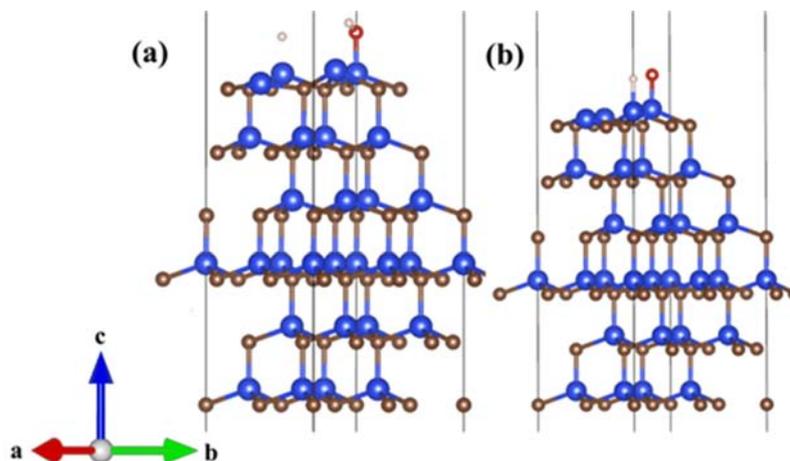
$$H^* \rightarrow 1/2H_2 \qquad (3)$$

FIG. 3 (a) OH* and H* produced from the absorbed water molecule are both absorbed on Si, and (b) O* and H* produced from OH* are both absorbed on Si.

TABLE II The absorption energies of the O and H atoms absorbed at different sites.

| Atom | Absorption sites | | E_r/eV |
	Before optimization	After optimization	
O	Si	Si	1.65
	h_1	h_1	0.65
	h_2	h_2	0
H	Si	Si	0
	h_1	h_1	1.71
	h_2	h_2	1.15

and the energy difference is 2.02 eV, which is a large value. This demonstrates that the reaction is almost unable to occur under ambient conditions and that the absorbed hydrogen atom is stable on the surface. In some studies, 6H-SiC was reported as the electrochemical catalyst for the hydrogen evolution reaction (HER) [17, 18], which requires a small ΔE value of the above reaction. According to the present calculation results, HER could not occur on the 6H-SiC(0001) surface due to the large ΔE value.

The radius of hydrogen is very small; thus, is it possible that the hydrogen intercalates into the lattice of SiC? Here, as shown in FIG. 4, the intercalated hydrogen atom is in the center of a cave surrounded by three silicon and three carbon atoms. Compared to the hydrogen absorbed on the silicon atom, its relative energy is approximately 3.76 eV, which is a large positive value and implies that the hydrogen atom could not insert into the SiC crystal lattice.

The hydrogen atom is absorbed on the top of the silicon atom, and it could hop to the neighboring silicon atom. With the NEB (Nudged energy band) method, the migration pathway is shown as the black arrow in FIG. 5(a), and the energy barrier is approximately 1.0 eV, as shown in FIG. 5(b), which implies that the
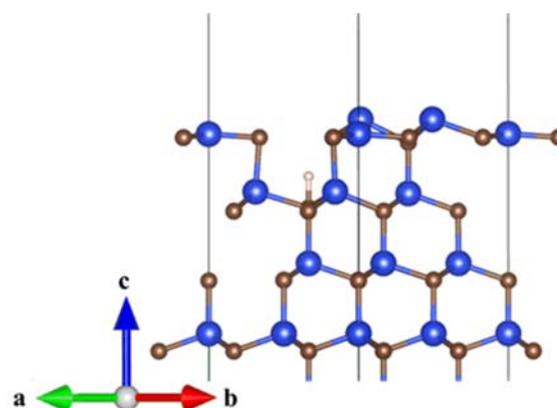

FIG. 4 The intercalated hydrogen atom is in the center of a cave surrounded by thee silicon and three carbon atoms.

hydrogen atom could diffuse onto the 6H-SiC(0001) surface.

Based on the above calculation results, the oxygen and water molecules could not be stable on the 6H-SiC(0001) surface and are dissociated into the absorbed oxygen atom, hydrogen atom and hydroxyl group. The charge density differences, which could be applied to investigate the chemical bonds between atoms, are shown in FIG. 6, and the blue and yellow isosurfaces represent the negative and positive values, respectively. For the absorbed oxygen atom, which is on the h_2 site, the electrons are transferred from three neighboring silicon atoms to the oxygen atom, which implies that the electron of the Si atom's dangling bond is expropriated. Then, the ionized Si atom would further weaken the stability of the SiC crystal, which is a covalent crystal, and some studies have proven that the SiC crystal could be oxidized to SiO_2 [7, 10, 11, 13, 14, 16].

For the absorbed hydrogen atom, the electron around the silicon atom is obviously reconstructed, and a co-
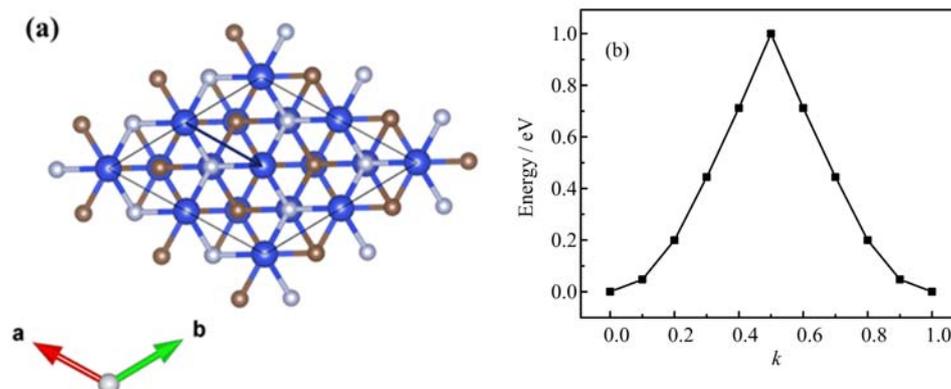
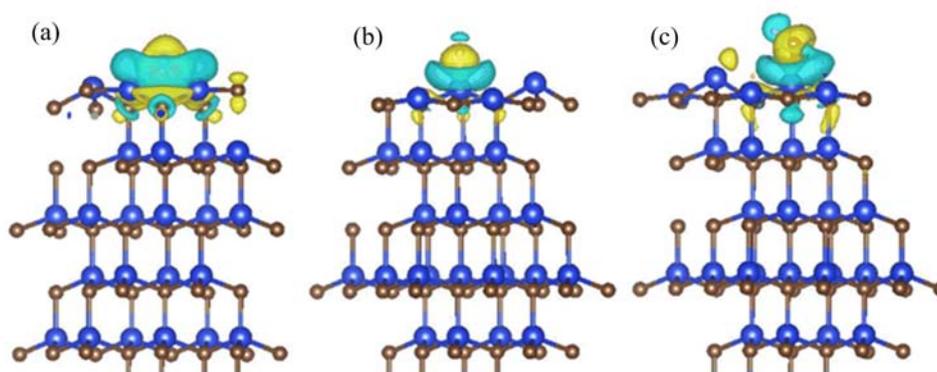FIG. 5 (a) The H* migration pathway and (b) the energy barrier.

FIG. 6 The charge density difference of (a) O*, (b) H* and (c) OH*.

valent bond Si−H is formed, with which the dangling bond of Si atom is saturated. The absorbed H atom and the three neighboring carbon atoms make up a tetrahedron around the silicon atom, which is similar to the SiC$_4$ tetrahedron in the SiC crystal. Then, the H terminated 6H-SiC(0001) surface is stable, consistent with previous experimental results [19]. Similar to the absorbed hydrogen atom, the absorbed hydroxyl group and the three neighboring carbon atoms form a tetrahedron around the silicon atom, and the isosurface demonstrates that the Si−O bond is covalent, which implies that the absorbed hydroxyl group could also stabilize the 6H-SiC(0001) surface.

In a low-humidity atmosphere, the O$_2$ is dissociated into O* on the 6H-SiC(0001) surface, which is absorbed on the h$_2$ site, and the SiC surface is further oxidized into SiO$_2$. In a high-humidity atmosphere, many water molecules are absorbed on the 6H-SiC(0001) surface, which are dissociated into OH* and H*, and they are both absorbed on the top of the Si atom. The OH* is further reversibly dissociated into O* and H*, which are also both absorbed on the top of the Si atom. Due to the absorbed hydrogen atom, O* from O$_2$ could be not at the h$_2$ site but on the top of Si site and may be further transformed into OH*, which implies the reaction

from SiC to SiO$_2$ could be impeded. The absorbed H*, which saturates the dangling Si bond, clearly strengthens the stability of the 6H-SiC(0001) surface. Then, in the atmosphere with high humidity, such as the cutting process with water cooling, the 6H-SiC(0001) surface could be stabilized with absorbed H* and OH* from water molecule dissociation.

IV. CONCLUSION

In summary, for O$_2$ absorbed on the 6H-SiC(0001) surface, the O=O bond is spontaneously broken, and the dissociated O* is absorbed on the h$_2$ sites. The absorbed H$_2$O is dissociated into OH* and H*, which are both absorbed on the top of the Si atom, and the OH* is further reversibly dissociated into O* and H*, which are also both absorbed on the top of Si atom. The absorbed H* could stabilize the 6H-SiC(0001) surface in two ways: first, H* could saturate the dangling Si bond, and second, H* could force O* to move from the h$_2$ site to the top of the Si site and further transform it into OH*. Then, in a high-humidity atmosphere, such as a cutting process that uses water as the cooling liquid, the structural stability of the 6H-SiC(0001) surface could be improved.

V. ACKNOWLEDGMENTS

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