

Reaction mechanisms at 4H-SiC/SiO₂ interface during wet SiC oxidation

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Abstract

The reaction processes of wet oxidation at 4H-SiC/SiO₂ interfaces are investigated by performing electronic structure calculations within density functional theory. Our calculations demonstrate characteristic features of the reaction depending on the crystal orientation of SiC: on the Si-face the H₂O molecule is stable in SiO₂ and hardly reacts with SiC substrate, while the O atom of H₂O can form Si-O bonds at the interface of the C-face. We also find that at least two OH⁻ are necessary to form Si-O bonds at the interface on the Si-face, indicating that the oxidation rate on the Si-face is very slow compared with the C-face. These calculated results imply that the reaction processes depending on the orientation could be rate-limiting during wet SiC oxidation.

1. Introduction

SiC is one of the wide-band gap semiconductor materials, has attractive properties for applying in electronic devices operating under high power and high frequency conditions. Furthermore, the formation of native oxides in SiC enables us to fabricate electronic devices such as metal-oxide semiconductor field-effect transistors (MOSFETs) analogous to Si-based technology. However, it has been reported that there are large number of defect-related states in the energy gap, and these states result in low channel mobility in SiC-MOSFETs [1]. Since the oxidation of SiC dominates the reliability of SiC-MOSFETs, many experimental and theoretical studies have been carried out to understand the mechanisms of SiC oxidation [2-9]. Furthermore, it has also been reported that oxidation under wet conditions is effective to improve the quality of interface in MOSFETs. Although the effects of H₂O on the inversion channel mobility of MOSFETs and the difference of near-interface strain in SiO₂ between dry and wet oxidation have been discussed [2,9], the impacts of wet oxidation on physical structures and also the oxidation mechanisms under wet condition still remains unclear.

In our previous study, the reaction processes of dry oxidation at 4H-SiC/SiO₂ interfaces have been theoretically investigated on the basis of electronic structure calculations within density functional theory (DFT). We have revealed characteristic features of the reaction of O₂ molecule at the interface depending on the crystal orientation of SiC. In this

study, we extend our approach to investigate the reaction processes of wet oxidation at both Si-face and C-face interfaces. The physical origins of the orientation dependence are discussed on the basis of calculated energy barriers.

2. Calculation procedure

The calculations within DFT have been performed using the generalized gradient approximation [11] and ultrasoft pseudopotentials [12]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 25 Ry, which gives enough convergence of total energy. In this study, 4H-SiC/SiO₂ interfaces are simulated using (3 × 4) slab models consisting of five bilayers of SiC and two monolayers of SiO₂ and an approximately 7 Å vacuum region. We use Γ -point sampling in the Brillouin zone integration. As a representative of SiO₂ generated by thermal oxidation of SiC, we adopt cristobalite-like structure, which has been obtained by our previous calculations for the oxidation processes on SiC surfaces [7,8]. The energetics of the reaction is examined using the incorporation energy $E_{inc} = E_{tot} - E_{SiC/SiO_2} - n_{oxidant}\mu_{oxidant}$, where E_{tot} and E_{SiC/SiO_2} are the total energy of the interface with oxidant and that of initial 4H-SiC/SiO₂ interface, respectively. $n_{oxidant}$ and $\mu_{oxidant}$ is the number of oxidant and its chemical potential in the gas phase, respectively. Here, we take both H₂O and OH⁻ into account as an oxidant near the interface, since it has been reported that OH⁻ is easily formed from H₂O in SiO₂ with low reaction energies [3]. To explore the reaction energy barrier, we use the nudged elastic band (NEB) method [13].

3. Results and discussion

Figure 1 shows the geometries of metastable and stable structures hosting an H₂O or OH⁻ at Si-face and C-face 4H-SiC/SiO₂ interfaces. On both Si-face and C-face, the H₂O is stably located at open spaces in SiO₂ region as shown in Fig. 1(a). Table I shows the calculated E_{inc} for various geometries. This table indicates that the structure with the H₂O in SiO₂ is the most stable on the Si-face. The reaction energy of the H₂O is endothermic. Therefore, the H₂O hardly interact with SiC substrate on the Si-face even at 0 K. Our calculations indeed demonstrate that two OH⁻ attaching Si atoms of SiO₂ shown in Figs. 1(b) is necessary for the O atom to form Si-O-Si and H-C-OH bonds on the SiC substrate shown in Figs. 1(c). The dissociation of H₂O molecule is thus indispensable

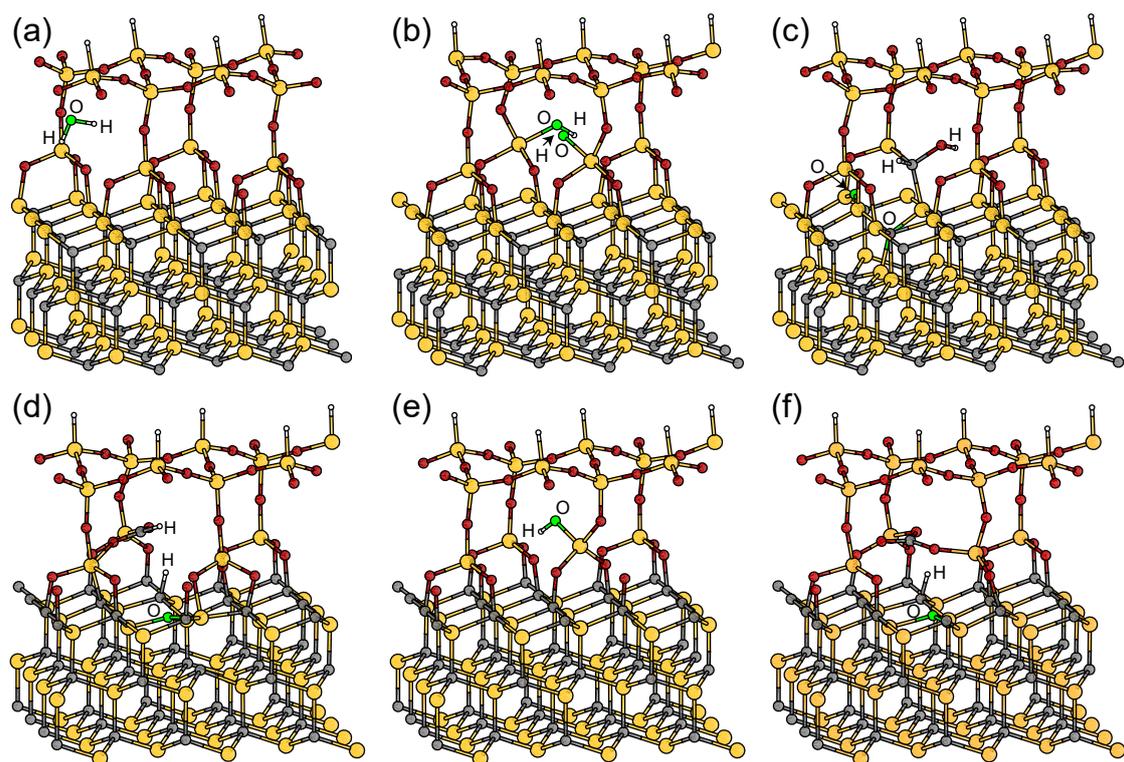


Fig. 1 Geometries of (a) H_2O in SiO_2 (Si-face), (b) two OH^\cdot in SiO_2 (Si-face), (c) Si-O-Si and H-C-OH bonds (Si-face), (d) Si-O-Si and O-CH-O bonds (C-face), (e) OH^\cdot in SiO_2 (C-face), and (f) Si-O-Si and CO_3 bonds (C-face) near the 4H-SiC/ SiO_2 interface. Empty and filled circles represent host Si and O atoms, respectively. The O and H atoms of oxidant H_2O are labeled.

for the reaction processes during wet Si oxidation on the Si-face. This feature could be one of possible origins for the low oxidation rate on the Si-face [10].

In contrast, the H_2O molecule on the C-face can form Si-O-Si and O-CH-O bonds at the interface shown in Fig. 1(d). The reaction energy is exothermic, suggesting that the reaction of H_2O molecule is energetically possible. We also find that a single OH^\cdot shown in Fig. 1(e) can interact with SiC substrate, resulting in the formation of Si-O-Si and CO_3 bonds [Fig. 1(f)]. The calculated energy barriers for the H_2O and OH^\cdot on the C-face obtained by the NEB method are 3.9 and 1.9 eV, respectively. The energy barrier for H_2O is large to

occur even under high temperatures. Therefore, the OH^\cdot mainly contribute to the formation of oxide on the C-face. It should be noted that the calculated energy barrier of OH^\cdot is comparable to experimentally reported activation energy (2.1 eV) on the C-face [4].

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Table I Calculated incorporation energy E_{inc} for various geometries involving an $\text{H}_2\text{O}/\text{OH}^\cdot$ at Si-face and C-face 4H-SiC/ SiO_2 interfaces. Values in parenthesis are the reaction energies of $\text{H}_2\text{O}/\text{OH}^\cdot$.

Orientation	Geometry	E_{inc} (eV)
Si-face	H_2O in SiO_2	-0.15
	Si-O-Si + CH_2	1.17 (-1.32)
	OH^\cdot in SiO_2	-0.27
	Si-O-Si + H-C-O	1.34 (-1.61)
	2 OH^\cdot in SiO_2	-0.44
	Si-O-Si + H-C-OH	-3.55 (3.11)
C-face	H_2O in SiO_2	-0.15
	Si-O-Si + O-CH-O + C-H	-0.76 (0.61)
	OH^\cdot in SiO_2	-1.54
	Si-O-Si + CO_3 + C-H	-2.06 (0.52)