

# Reactions of NO molecule with carbon-related defects at 4H-SiC/SiO<sub>2</sub> interface under dry oxidation conditions

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## Abstract

The reactions of NO molecule with carbon-related defects at 4H-SiC/SiO<sub>2</sub> interface are investigated by performing first-principles calculations. Our calculations demonstrate characteristic features of the reaction depending on the orientation. On the Si-face, the dissociation of C-C bond and the formation of CO<sub>2</sub> molecule preferentially occur, which is most stable state at 4H-SiC/SiO<sub>2</sub> interface. On the other hand, C=C bond changes into C-C bond with the formation of CO<sub>2</sub> molecule on the C-face. Furthermore, the reaction energy for CO<sub>2</sub> formation on the Si-face is higher than that on the C-face. These results suggest that the reaction of NO molecule after the generation of carbon-related defects at the Si-face interface is more effective for the degradation than that on the C-face.

## 1. Introduction

4H-SiC is a key material for applying in power electronics devices because of its superior physical properties. Furthermore, the formation of native oxides SiO<sub>2</sub> by thermal oxidation enables us to fabricate metal-oxide-semiconductor field-effect transistors (MOSFETs) in SiC. However, the interface between 4H-SiC and SiO<sub>2</sub> interface obtained by thermal oxidation has large number of defects, which degrade the performance of SiC-MOSFETs such as channel mobility. Since the quality of 4H-SiC/SiO<sub>2</sub> interface is crucial to commercialize SiC power devices, many experimental and theoretical efforts have been devoted to clarify SiC-oxidation mechanisms and also the origins of degradation at the resultant 4H-SiC/SiO<sub>2</sub> interface. From theoretical viewpoints, the electronic states of C=C double-bond defects have been investigated as a possible origin for the degradation and these defects could be passivated by changing the C=C double bond to a C-C single bond [1]. On the other hand, the effects of NO annealing on the interface state have been discussed. Experiments using C-V measurements for samples with NO-POA has clarified that the interface states existing at oxidized interface decreased by NO annealing, and the process is more effective on the Si-face than that on the C-face [2,3]. However, the relationship between NO-annealing and MOS channel mobility is still unclear. This is because, the behavior of NO molecule near the oxidized interface is not yet clarified on the atomic scale.

Previously, we investigated the SiC-oxidation reaction pro-

cesses during dry and wet oxidation on the basis of first-principles calculations [4,5]. For dry process, the formation and desorption of CO molecule easily occur at the both Si- and C-face 4H-SiC/SiO<sub>2</sub> interfaces and the interfaces are stabilized. Furthermore, we have found the formation of C-C and C=C bonds at the interface during dry oxidation [4]. In this study, we extend our approach to investigate the reactions of NO molecule at the oxidized 4H-SiC/SiO<sub>2</sub> interface under dry conditions to clarify the effects of NO molecule on carbon-related defects at the interface. The NO contribution to interface states and its orientation dependence are also discussed.

## 2. Methodology

We simulate both Si-face and C-face 4H-SiC/SiO<sub>2</sub> interfaces by using  $c(2\sqrt{3}\times 3)$  slab models consisting of four 4H-SiC bilayers, two SiO<sub>2</sub> monolayer and an approximately 10 Å vacuum region. A cristobalite-like structure is used as a representative of SiO<sub>2</sub> generated by thermal oxidation of SiC, which have been obtained by our previous calculations [4-6]. Similar atomic configurations at 4H-SiC/SiO<sub>2</sub> interfaces have also been reported in previous calculations. H atoms are used to terminate the bottom and top surfaces of the slab and the lower bilayers of slab models are fixed at ideal positions. Our calculations are performed within the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional [7]. We employ norm-conserving (ultrasoft) pseudopotentials to describe electron-ion interaction for Si and H (C, O and N) atoms [8,9]. The plane-wave basis set with a cutoff energy of 30.25 Ry is used to expand the valence wave functions. The calculations have been performed using Tokyo *Ab initio* Program Package (TAPP) [10].

Here, we consider NO molecule as an annealing species near the interface. The energetics of 4H-SiC/SiO<sub>2</sub> interface is examined using the incorporation energy  $E_{\text{inc}}$  of NO molecule which is defined as

$$E_{\text{inc}} = E_{\text{total}} - E_{\text{defect}} - E_{\text{NO}}, \quad (1)$$

where  $E_{\text{total}}$  and  $E_{\text{defect}}$  are total energy of the 4H-SiC/SiO<sub>2</sub> interface with NO molecule and that including carbon-related defects calculated from *ab initio* calculations, respectively.  $E_{\text{NO}}$  represent the total energy of NO molecule in the gas phase. In addition, we introduce the reaction energy  $E_{\text{rc}}$ , which is given by the difference in  $E_{\text{inc}}$  between the initial and final interface structures of the interfacial reaction.

### 3. Results and Discussion

Figures 1(a) and 1(b) shows the geometries corresponding to the initial structures for the reaction at the Si- and C-face interfaces, respectively. The NO molecule is stably located at the open space of the SiO<sub>2</sub> region, and therefore these structures can be regarded as initial states for the reaction of NO. The incorporation energies  $E_{inc}$  are 0.93 and 0.58 eV for Figs. 1(a) and 1(b), respectively. On the Si-face, we find the stable atomic configuration consisting of CO<sub>2</sub> molecule in SiO<sub>2</sub> region and Si<sub>4</sub>-N (four Si-N bonds) and Si-O-C bonds as a final state of the NO reaction. Another stable structure consisting of Si<sub>3</sub>-N and Si-O-C bonds and CO molecule is also found at the interface on the Si-face. The calculated  $E_{inc}$  and  $E_{rc}$  of their structures are shown in Table 1. These results indicate that NO molecule is favorable species for the dissociation of C-C bond. It is found that  $E_{rc}$  for CO<sub>2</sub> formation (8.28 eV) is higher than that of CO molecule (5.91 eV), suggesting that the formation of CO<sub>2</sub> molecule shown in Fig. 1(c) is more preferable than that of CO molecule on the Si-face.

In contrast, the formation of CO<sub>2</sub> molecule with C-C and Si-N-C bonds is found as a stable structure on the C-face. We also find a different atomic configuration consisting of O-N-C bond and CO<sub>2</sub> molecules. The calculated  $E_{inc}$  and  $E_{rc}$  for these geometries are also shown in Table 1. These values demonstrate that the formation of C-C bond shown in Fig. 1(d) is stabilized compared with that of O-N-C bond. It is thus suggested that structural change of the C=C bond into single C-C bond is thermally activated, which agree with previous calculations [1].

Indeed,  $E_{rc}$  for the formation of the geometry shown in Fig. 1 (d) is 3.20 eV and lower than that of the geometry shown in Fig. 1 (c). The results indicate that NO annealing is more effective for the reduction of carbon-related defects on the Si-face than that on the C-face, which qualitatively consistent with the experiments [3].

### 4. Conclusion

We found characteristic features of the reaction of NO molecule with carbon-related defects at the 4H-SiC/SiO<sub>2</sub> interface. On the Si-face, C-C bond dissociated, and CO<sub>2</sub> molecule is generated in SiO<sub>2</sub> region with Si<sub>4</sub>-N and Si-O-C bonds formation. On the other hand, the formation of CO<sub>2</sub> molecule with C-C and Si-N-C bonds easily occur on the C-face. The calculated reaction energies  $E_{rc}$  of these geometries are 8.28 and 3.20 eV on the Si- and C-faces, respectively. Therefore, NO molecule is effective for the reduction of carbon-related defects at both Si- and C-face 4H-SiC/SiO<sub>2</sub> interfaces. Furthermore, calculated  $E_{rc}$  also indicate that the interface after NO annealing on the Si-face is more stable compared with that on C-face, which qualitatively consistent with the experiments. These results may also lead to better understanding of atom-scale mechanism of NO annealing, which would be expected to improve the SiC MOS-interface.

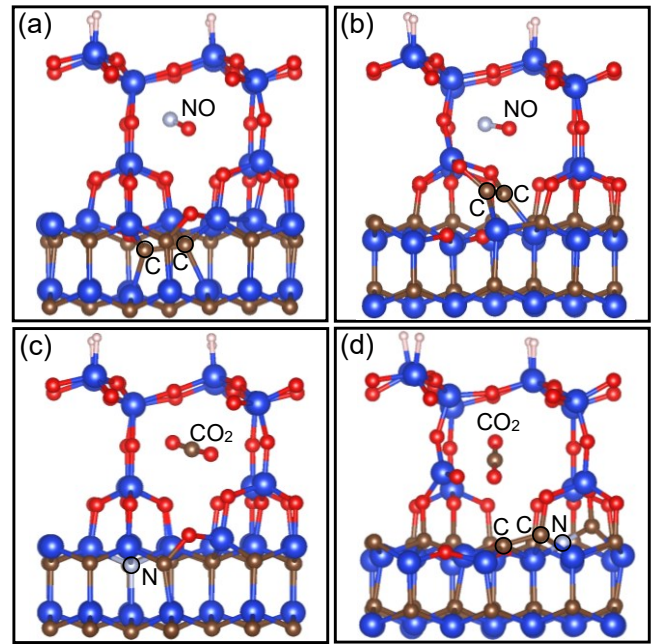


Fig. 1 Perspective atomic geometries of (a) C-C bond and NO molecule at Si-face interface, (b) C=C bond and NO molecule at C-face interface, (c) Si<sub>4</sub>-N and Si-O-C bonds and CO<sub>2</sub> molecule at Si-face interface, (d) C-C and Si-N-C bonds and CO<sub>2</sub> molecule at C-face interface. Blue, brown, red, pink and purple circles denote Si, C, O, H and N atoms, respectively.

Table 1 Calculated incorporation and reaction energies ( $E_{inc}$  and  $E_{rc}$ ) for various geometries at Si- and C-face 4H-SiC/SiO<sub>2</sub> interfaces. Positive value in  $E_{rc}$  means exothermic reaction.

Orientation	Geometry	$E_{inc}$ [eV]	$E_{rc}$ [eV]
Si-face	C-C + NO	0.93	-
	Si <sub>4</sub> -N + Si-O-C + CO <sub>2</sub>	-7.35	8.28
	Si <sub>3</sub> -N + Si-O-C + CO	-4.98	5.91
C-face	C=C + NO	0.58	-
	C-C + Si-N-C + CO <sub>2</sub>	-2.62	3.20
	O-N-C + CO <sub>2</sub>	-2.41	2.99

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