

A first principles study on the C=C defects near SiC/SiO₂ interface: Defect passivation by double bond saturation

Nobuo Tajima,^{1,2} Tomoaki Kaneko,^{1,2} Takahiro Yamasaki,^{1,2} Jun Nara,^{1,2} Tatsuo Schimizu,³
Koichi Kato,⁴ and Takahisa Ohno^{1,2,4}

¹WPI-Center for Materials Nanoarchitectronics, National Institute for Materials Science,
1-1, Namiki, Tsukuba, Ibaraki, 305-0044, Japan

²Materials Research Consortium for Energy Efficient Electronic Devices (MARCEED),
1-1, Namiki, Tsukuba, Ibaraki, 305-0044, Japan

³Corporate R & D Center, Toshiba Corporation, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki, 212-8582, Japan

⁴Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
E-mail: TAJIMA.Nobuo@nims.go.jp

Abstract

We performed first principles calculations to study the C=C defects near SiC/SiO₂ interface, and demonstrated that the intra-gap defect levels could be removed by changing the C=C double bond to a C-C single bond.

1. Introduction

Silicon carbide (SiC) is a suitable material for power electronics in view of its wide bandgap, high electron mobility, and high thermal conductivity. Besides this fact, SiC can be thermally oxidized to form an oxide layer, which makes SiC attractive as a base material for producing metal oxide semiconductor (MOS) devices. The SiC devices of current technology do not have acceptable performance however, because of problems such as channel mobility degradation and threshold voltage instability. These problems are attributed to defects around the SiC/SiO₂ interface which form defect states densely in the band gap of the SiC/SiO₂ system [1]. As a defective element of SiC/SiO₂ interface, sp² carbon species have been detected experimentally [1], which are produced as the remainder of the SiC oxidation. Carbon clusters with C=C bonds are thus thought to have some contributions to the defect state density [2].

In the present study, we perform first principles calculations to investigate the SiC/SiO₂ interface with the C=C defects as a simplest representative of the sp² carbon species. As described elsewhere, this defect can have defect levels in the band gap of the SiC/SiO₂ system [3]. We discuss an effective way to eliminate these intra-gap states based on the results of first principles calculations.

2. Computational Details

A model of 4H-SiC(0001)/SiO₂ interface was produced first, and then a pair of -O- atoms in this model was replaced with a carbon dimer to obtain interface models with a C=C dimer defect. We followed the theoretical study by Devynck et al. [4] to build the interface model of 4H-SiC(0001)/SiO₂. The model consists of an amorphous SiO₂ layer placed on an SiC substrate of 3 x 2√3 periodicity with eight bilayer thickness (Fig.1, upper part). The surface of the SiO₂ layer was terminated by Si-H groups, and the slabs were separated by the vacuum layer with thickness of

more than 15 Å. Geometries of model structures were optimized with the bottom three SiC bilayers fixed.

We employed density functional theory within generalized gradient approximation (GGA) for geometry optimization, while we used hybrid density functional theory (HSE06 functional) for electronic structure calculation. Ultrasoft pseudo potential was used for C and O atoms, and norm conserving pseudo potentials were used for H and Si atoms. The cutoff energies of wave function and charge density were chosen as 25 Ry and 255 Ry, respectively. Monkhorst-Pack mesh and uniform mesh of 2x2 size were employed for k-point sampling in the geometry optimizations and electronic structure calculations, respectively. The cell size was set to the calculated lattice constants of bulk 4H-SiC (a = 3.097 and c = 10.125 Å).

First principles simulator PHASE/0 was used for these calculations [5].

3. Calculated Results

To clarify the band alignment of the 4H-SiC/SiO₂ system, the calculated LDOS for the defect free interface model is presented in Fig. 1. With the higher valence band maximum (VBM) and lower conduction band minimum (CBM) of SiC than those of SiO₂, the band gap of the entire SiC/SiO₂ system is that of SiC, with a gap energy of 3.29 eV.

Eleven different model structures of C=C defects were obtained by replacing the O...O pairs nearer than 3 Å with a carbon dimer. Their structural parameters, relative energies, and the levels of defect states are listed in Table I. The carbon dimers in the model structures can be characterized as a distorted π bonded dimer: The central >C=C< bonds are mostly twisted considerably (see θ in Table I, the Si-C-C-Si dihedral angle), and the C-C bonds are somewhat longer than a typical C=C double bonds (~ 1.33 Å, calculated for ethylene).

The calculated data show that the model structures have different defect levels (see E_O and E_U in Table I, the levels of highest occupied and lowest unoccupied defect states, respectively, relative to the VBM of SiC), probably reflecting diverse local structures around the C=C defects. Many of the structures have defect levels in the band gap of SiC: model structures **1,2,4,5,9,10**, and **11** have occupied levels

higher than the VBM of SiC; the model structures **9** and **10** have unoccupied levels lower than the CBM of SiC. These data suggest that the C=C defects should have contributions to the experimentally observed defect state densities for the band gap energy region of SiC [1]. The highest occupied defect state has a character of σ bonding orbital on the C-Si bond, while the lowest unoccupied defect state has a character of π^* orbital on the C=C bond. As a whole, the structures with larger θ tend to have higher occupied defect states and lower unoccupied defect states.

The defect states in the band gap regions are known to damage the performance of SiC-MOS devices by worsening the channel mobility and threshold voltage stability [1]. Eliminating these intra-gap defect states by some means is expected to improve the device performance possibly. One of the ways to remove the intra-gap state would be to change the C=C double bond to a C-C single bond by some chemical reactions. It is well known that the sp^3 systems have wider HOMO-LUMO gap than the corresponding sp^2 systems in general. We checked reactions of the C=C center of the defect model structures with H_2 and F_2 molecules to form CH-CH and CF-CF bonds, respectively.

Fig. 2 shows the results obtained using the model structures **2** and **9**, which were picked up as representatives of the 11 model structures. The reactions to form CH-CH and CF-CF lower the levels of highest occupied defect states, and raise the levels of the lowest unoccupied defect states. As a result of these changes, the occupied intra-gap defect state for **2** and **9** become lower than the VBM of SiC, and the unoccupied intra-gap defect state **9** become higher than the CBM of SiC (the unoccupied defect state of **2** is already higher than the CBM even without reacting with H_2 or F_2). The C=C center in the interface models react exothermically with H_2 and F_2 : reaction energies calculated with the model structures **2** and **9** are -2.2 and -3.0 eV, respectively, for the H_2 reaction, and -3.2 and -4.4 eV, respectively for the F_2 reaction. The reaction energies calculated with the 11 model structures are all negative definitely, ranging in -1.2 to -3.0 eV for the reactions with H_2 , and -2.1 to -5.0 eV for the reactions with F_2 . If we could react F_2 and H_2 molecules selectively with the C=C center, we would be able to eliminate intra-gap defect state of the 4H-SiC/SiO₂ system.

4. Summary

We performed first principles calculations to study the C=C defects in the oxide layer near the SiC/SiO₂ interface. These calculated results revealed that the defect of this type can have occupied and unoccupied states in the band gap of the SiC. We have demonstrated that these defect levels could be removed from the band gap by changing the C=C double bond to a C-C single bond via reactions with molecules F_2 and H_2 .

Acknowledgement

The authors would like to thank T. Hatakeyama (AIST) and T. Umeda (Tsukuba Univ.) for valuable discussions. A portion of this research was partly supported by MEXT within "Strategic Programs for Innovative Research" Field

No. 4 (Project ID: hp150212), and the priority issue 6 of the FLAGSHIP2020 (Project ID: hp160226).

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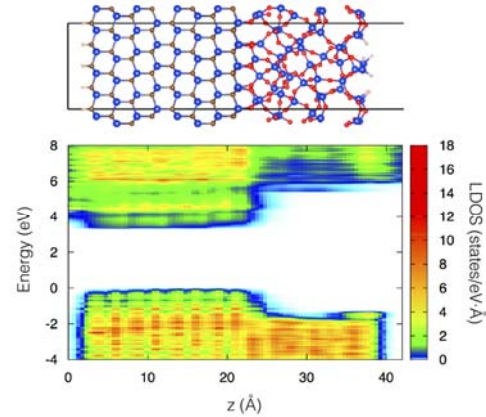


Fig.1. Model structure of 4H-SiC/SiO₂ and the calculated LDOS. Colors of atoms: blue (Si), brown (C), red (O), and gray (H).

Table I. Calculated results for the models with C=C defects

| | $z(\text{\AA})$ | $\Delta E(\text{eV})$ | $d_{CC}(\text{\AA})$ | $\theta(\text{deg.})$ | $E_O(\text{eV})$ | $E_U(\text{eV})$ |
|-----------|-----------------|-----------------------|----------------------|-----------------------|------------------|------------------|
| 1 | 2.386 | 1.42 | 1.393 | 51.3 | 0.5 | 3.4 |
| 2 | 2.393 | 1.15 | 1.387 | 12.6 | 0.1 | 3.5 |
| 3 | 3.084 | 0.00 | 1.382 | 3.3 | -0.4 | 4.2 |
| 4 | 3.115 | 1.02 | 1.392 | 27.6 | 0.1 | 3.6 |
| 5 | 3.348 | 1.64 | 1.397 | 35.0 | 0.2 | 3.5 |
| 6 | 4.612 | 0.84 | 1.391 | 12.8 | -0.6 | 4.1 |
| 7 | 4.952 | 0.12 | 1.366 | 24.2 | -0.2 | 4.2 |
| 8 | 5.028 | 1.40 | 1.384 | 42.8 | 0.0 | 3.8 |
| 9 | 5.292 | 1.76 | 1.397 | 77.2 | 0.7 | 3.0 |
| 10 | 7.219 | 1.24 | 1.413 | 58.2 | 0.1 | 3.2 |
| 11 | 7.925 | 0.92 | 1.385 | 56.1 | 0.1 | 3.5 |

z : distance of the defect center from the interface, ΔE : relative total energy, d_{CC} : C-C bond length, θ : Si-C-C-Si dihedral angle (averaged over combinations of Si), E_O and E_U : levels of the highest occupied and the lowest unoccupied defect states relative to the VBM of SiC (see Fig.1). Note that the CBM of SiC is located 3.3 eV above the VBM of SiC.

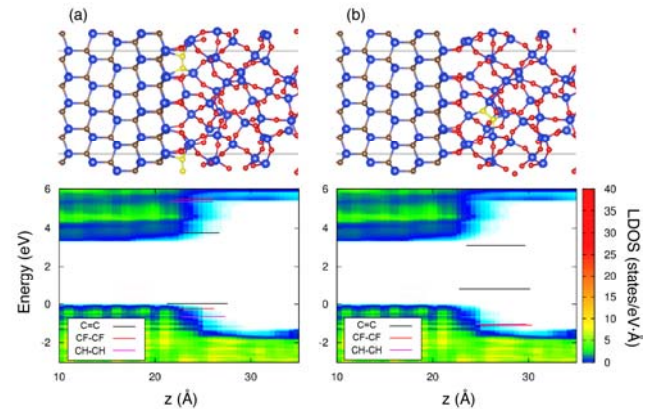


Fig.2. Defect levels calculated for a C=C defect and its passivated forms CH-CH and CF-CF. Model structures **2** and **9** (see Table I) were used to obtain the data in (a) and (b), respectively.