First-Principles Molecular Dynamics Simulation of Oxide Layer for SiC Devices

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Silicon carbide semiconductor devices are expected to be used in severe environments such as outer space and nuclear power plants. However, the performance of SiC devices is much lower than the theoretically expected values. This is considered to be attributed to defects at the SiO_2/SiC interface that degrades the electrical performance of the devices. It is important to construct the amorphous SiO_2 (a-SiO_2) structure on SiC to simulate the actual device interface structure on the computer. To generate a-SiO_2/SiC interface structure, the heating and quenching calculation was performed using the first-principles molecular dynamics (MD) calculation. The slab model is used for the initial structure of calculation. It has a size enough to generate the a-SiO_2/SiC interface structure. After heating and quenching calculation, SiO_2 layer of this model became amorphous characteristics. The simulation result does not become a defect-free structure at interface. There is a defect with five coordinations Si at the interface. This coordination defect disappears when the quenching speed slow down from –2000 K/ps to –500 K/ps. We performed the dynamical simulation of the SiO_2/4H-SiC C-face interface oxidation process using first-principles MD method. The MD simulation is carried out at 2500 K. The O_2 molecule is dissociated in the SiO_2 layer or by Si atoms at the SiO_2 interface. The O atom of the O_2 molecule oxidized the C atom at the SiC interface and formed Si-C-O complex.

Keywords: SiC device, first-principles, molecular dynamics, interface defect, oxidation process

1. Introduction

Silicon carbide (SiC) semiconductor devices are expected to be used in severe environments such as outer space and/or nuclear power plants. The performance of SiC metal-oxide-semiconductor (MOS) devices to date is low enough as compared with theoretical performance expected. This is considered to be attributed to defects generated at the SiO_2/SiC interface that degrade the electrical characteristics of MOS devices. However, it is not clear at present what kind of defects affect the degradation of electric characteristics. Although a lot of researchers have been done for analyzing the relation between physical structure near the interface and electrical characteristics in actual MOS devices, the details are not clear at present. The aim of our study is to know the relation between physical structure and electrical characteristics at the interface by using large scale simulation. We try to generate a-SiO_2 layers in the atomic network model at the interface because the oxide-layer in actual SiC MOS devices has an amorphous characteristic. In the last year, the SiO_2 layers of the calculation results almost became an amorphous characteristic [1] using middle scale model. However, atomic network with defect was not generated at interface in the middle scale model though it was frequently observed in the actual devices.

In this work, a large-scale slab model was prepared on the basis of an atomic network of beta quartz (β-SiO_2) on 4H-SiC crystal and theoretical structures simulated for the interface in the actual SiC MOS devices were successfully obtained on the Earth Simulator by heating and quenching calculation for the slab model. It is also important to understand the thermal oxidation process at the SiO_2/SiC interface to improve characteristics of SiO_2/SiC interface. The oxidation process on the C-face is very interesting because its oxidation rate is ten times higher than that of the Si-face [2] and the channel mobility on a C-face MOSFET is higher than that on a Si-face one. We report the dynamical simulation results of the oxidation process on the C-face and discuss the difference in the process between the Si-face and the C-face.

2. Simulation result

2.1 Simulation calculation of real device interface that uses large-scale interface model

Last year, we obtained the SiO_2 layers with an amorphous characteristics [1] using 444 atoms middle-scale model. However, the defect at the interface was not induced, though it was observed in the actual devices. The aim of this report is to produce the theoretical interface involving the defects at the interface and to know the relation between physical structure and electrical characteristics at the interface by using large-scale simulation.

A simulation for the *a*-SiO_2/SiC interface in the actual SiC MOS devices was carried out on computer using the first-principles MD calculation, in which Vienna *ab initio* Simulation Package (VASP) [3–5] was employed as a calculation code. Prior to the calculation, a large-scale slab model using 1017 atoms (693 atoms at the heating and quenching calculation) was prepared on the basis of an atomic network for beta quartz (β-SiO_2) on 4H-SiC crystal. The Si atoms at the top of β-SiO_2 and the C atoms at the bottom of 4H-SiC crystal were saturated by H atoms. By applying the heating and quenching method to the large-scale slab model, a theoretical structure around the *a*-SiO_2/SiC interface was obtained on computer. Figure 1 exhibits the temperature profiles of the heating and quenching method for the simulation. Three different types of temperature profiles are applied. The total energy of large-scale model is also plotted in the same figure.

In the beginning, the SiO_2 layer has been melted by 2 ps at the temperature of 4000 K. During the melting process, SiC atoms of the substrate are kept frozen except 2 interface layers. Surface Si atoms of SiO_2 layers are saturated with H atoms. Both the Si and the H atoms are also kept frozen at melting process. Next, the model cooled down to the temperature of 3500 K. Afterwards, the H atoms are removed from models and surface Si atoms are melted. Then the model was continuously annealed for 2 ps. Finally, the model was quenched to the room temperature using several quenching rates.

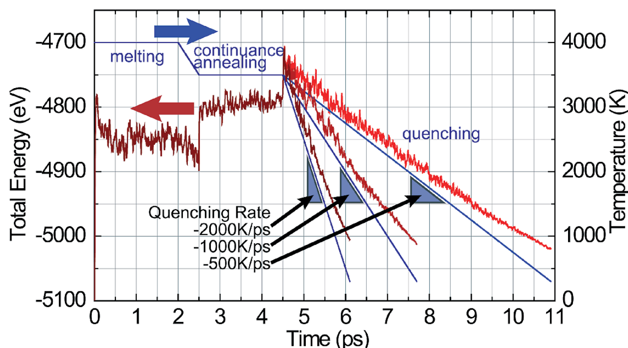

Fig. 1 The temperature profile of the heating and quenching process and the transition of total energy.

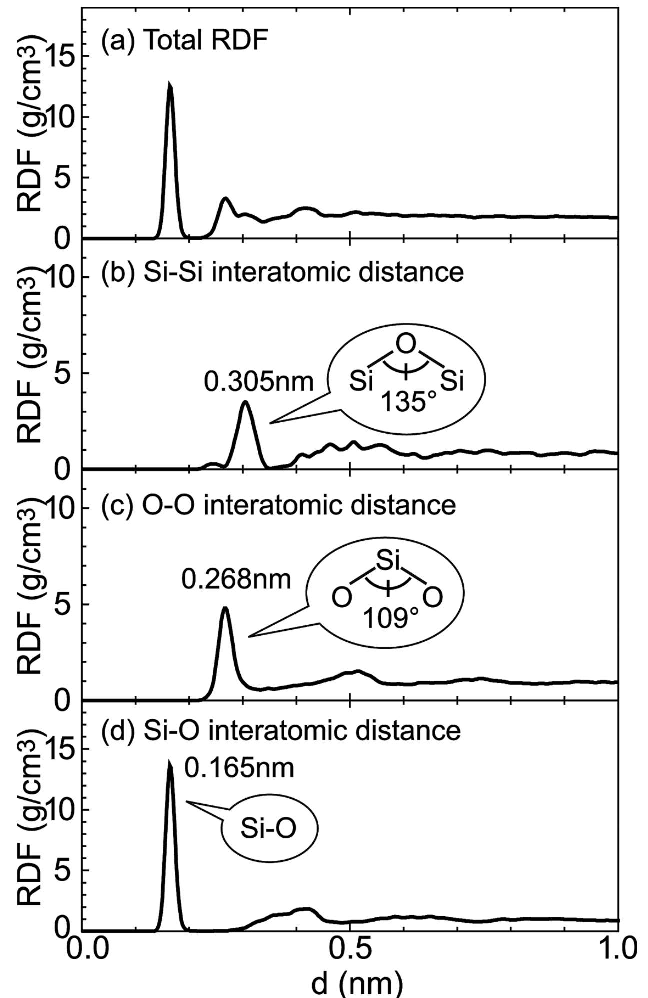

Fig. 2 Total and partial RDF of the SiO_2 layers at room temperature with the quenching rate of –2000 K/ps.

In order to estimate the distribution of the SiO_2 layers of theoretical structure obtained, radial pair distribution function (RDF) was applied. Figure 2 shows the total and partial RDF of the SiO_2 layers at room temperature with the quenching rate of –2000 K/ps. No long range order was seen for the theoretical structure. On the contrary, the short range order was observed. The Si-O bond length is 0.165 nm and the O-Si-O bond angle is 109 deg. As seen in Fig. 3, the average bond angle of Si-O-Si increases from 135 deg to 140 deg with the decrease of quenching rate from –2000 K/ps to –500 K/ps. It was found that the average bond angle for the quenching rate of –500 K/ps is close to that of silica glass (145±10 deg).

As for the theoretical structure at the interface, the several kinds of defects such as a Si dangling bond, Si-Si bonds and a Si atom with the coordination number of 5 are produced at the interface. It is not explain well with reasons that these defects are generated at the interface of theoretical structure during the heating and quenching procedures. However the composition ratio of O to Si (O/Si ratio) at the interface is high enough as compared with that in the SiO_2 layers, which

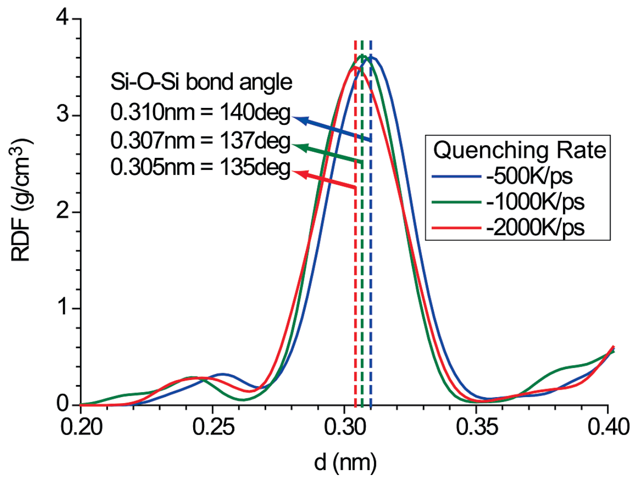

Fig. 3 The Si and Si interatomic distance at the several quenching rate.

indicates following thing. As compared with Si in SiO_2 layers, O links easily with the exposed bonds of Si atoms at the interface involving 4H-SiC substrate during the process. Therefore these defects, especially for the Si-Si bond or Si dangling bond, would reduce the excess oxygen at the interface and improve the O/Si ratio to a normal value of 2. As for the behavior of a Si atom with the coordination number of 5, the structure disappeared when the quenching rate slow down from –2000 K/ps to –500 K/ps (Fig. 4).

2.2 Dynamical simulation of SiO_2/SiC interface oxidation process

The calculations have been performed by the VASP with plane waves, supercells, and the projector augment wave method [3–5]. Only the gamma point is used for the sampling Brillouin zone. The SiO_2/4H-SiC(000-1) (C-face SiC) interface model is determined as follows. We use multiplied by $\sqrt{3}$ 1 × 1 C-face SiC as the SiC region initial structure. The number of atoms in the unit cell of this interface model is 78. Interface Si atoms of SiO_2 region bond to C atoms of SiC region. One interface Si atom bonds to three C atoms of SiC interface. This Si terminated C-face model is stable under the 3500K MD run. The band gap of this interface model is the same as 4H-SiC bulk one. This means interface states do not exist in this interface model. Then we multiplied by 2 × 2 this small interface model.

The slab model is used for SiO_2/SiC interface simulation with β-tridymite as the SiO_2 initial structure and multiplied by $2\sqrt{3}$ 1 × 1 4H-SiC(000-1) C-face as the SiC region initial structure. In the SiC regions, 16 atomic layers are used for 4H-SiC and ten atomic layers are used in the SiO_2 region. The number of atoms in unit cells with the SiO_2/4H-SiC(000-1) interfaces is around 280. In the simulation, all ten SiO_2 layers and the eight layers of 4H-SiC nearest to the interface are free. The remaining eight atomic layers of 4H-SiC have a bulk crystal structure. Dangling bonds on opposite sides of the interface, Si dangling bonds of SiC,

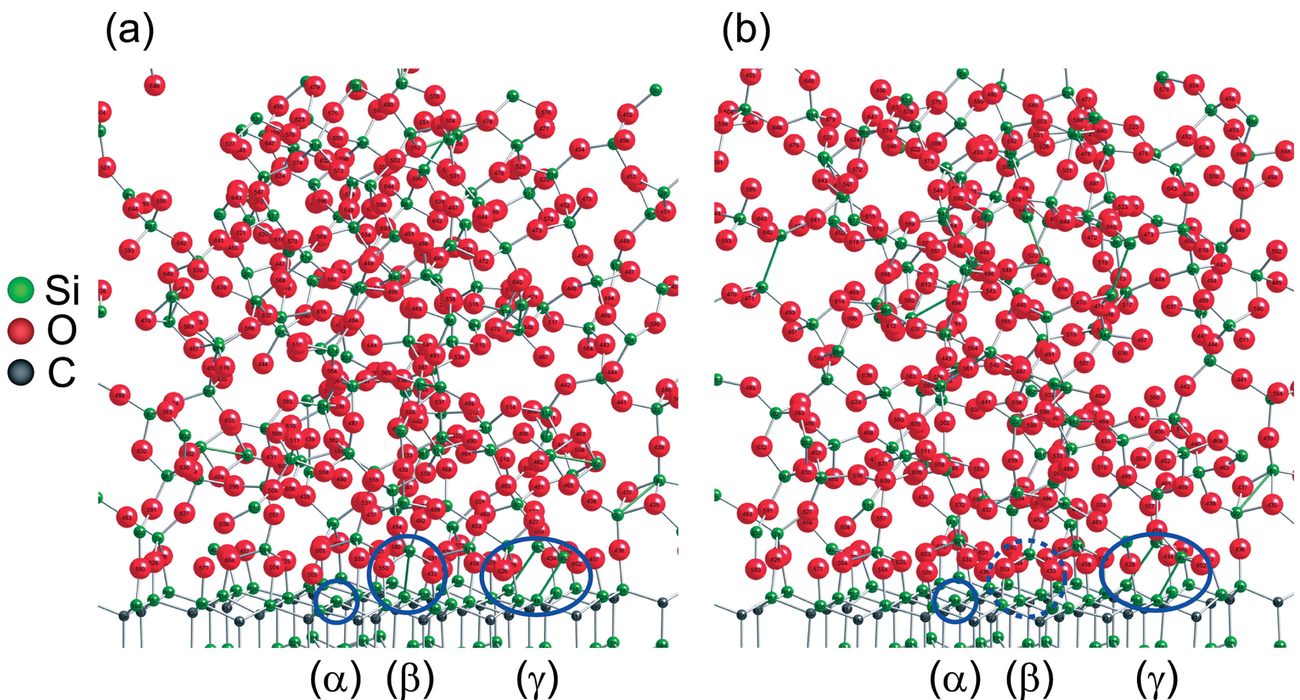

Fig. 4 The atomic structure at the a-SiO_2/SiC interface. The rate of the rapid quenching to the room temperature is (a) –2000 K/ps and (b) –500 K/ps, respectively. These are three kinds of defect is observed at the interface. (α) is a Si dangling-bond, (β) is a Si-Si bond and five coordination Si, and (γ) is Si-Si bond. The structure (β) disappeared when the quenching rate slow down from –2000 K/ps to –500 K/ps.

are saturated with H atoms. The heating and quenching method was carried out to prepare the initial SiO_2/4H-SiC(000-1) C-face model interface structure. The heating temperature and heating time are 3500 K and 3.0 ps. The time step is 1 fs and temperature is controlled by velocity scaling in every step. Quenching was carried out to 0 K at the rate of –1000 K/ps. In this initial interface model structure, there are no transition oxide layers, defects or dangling bonds at the SiO_2/SiC interface but the tridymite structure remains. In the simulation of SiO_2/4H-SiC(000-1) C-face oxidation process, we introduce the Si vacancy into the SiC layer near the interface in order to trigger the oxidation process.

We put the first O_2 molecule in the empty sphere of the SiO_2 layer (Fig. 5(a)). The O_2 molecule is bonded to interface Si atoms in the SiO_2 layer (Fig. 5(b)). Then, the bond of the O_2 molecule is broken. One oxygen atom retains its bond with the Si atom and the other oxygen atom moves to the carbon interface atom (Fig. 5(c)). The oxygen atom and interface carbon atom reacts and a CO molecule is formed (Fig. 5(d)). The CO molecule reacts with the oxygen atom having a dangling bond in the SiO_2 layer and forms a CO_2 molecule (Fig. 5(e)). The CO_2 molecule reacts with the interface carbon atom and a C-C-O-Si bridge finally formed (Fig. 5(f)). In the course of reactions, the interface Si atom in the SiO_2 layer moves to the Si vacancy position (Fig. 5(f)). A tenth O_2 molecule is added at 72 ps. Two CO_2 molecules and a CO molecule are formed at 80 ps. The rest of C atoms at the interface form partially oxidized complexes, for example O-C-C and O-C-C-C complexes (Fig. 5(g)).

3. Conclusion

A simulation for the *a*-SiO_2/SiC interface in the actual SiC MOS devices was carried out on computer using the first-principles MD calculation. Three different types of temperature profiles for the heating and quenching method are applied. The short range order was observed from the RDF analysis for the SiO_2 layers of theoretical structure obtained. The bond angle of Si-O-Si is observed to be 135 deg, 137 deg and 140 deg with the quenching rate of –2000 K/ps, –1000 K/ps and –500 K/ps, respectively. The Si-O-Si bond angle is close to the value of silica glass at the slow quenching rate. The coordination defect at the SiO_2/SiC interface disappeared with decreasing of the quenching rate to room temperature from –2000 K/ps to –500 K/ps. It is assumed that a low quenching rate is necessary at the heating and quenching calculation to obtain the more stable atomic network model of the *a*-SiO_2/SiC interface from the result of the extension of the Si-O-Si bond angle and the disappearance of the coordination defect at the interface. We performed the dynamical simulation of the SiO_2/4H-SiC C-face interface oxidation process using first-principles MD based on plane waves, supercells, and the projector augmented wave method. The slab model has been used for the simulation. The molecular dynamics simulation is carried out at 2500 K. The O_2 molecule is dissociated in the SiO_2 layer or by Si atoms at the SiO_2 interface. The O atom of the O_2 molecule oxidized the C atom at the SiC interface and formed Si-C-O complex. A formed CO_X molecule in the C-face oxidation is more easily diffused than that in the Si-face oxidation.

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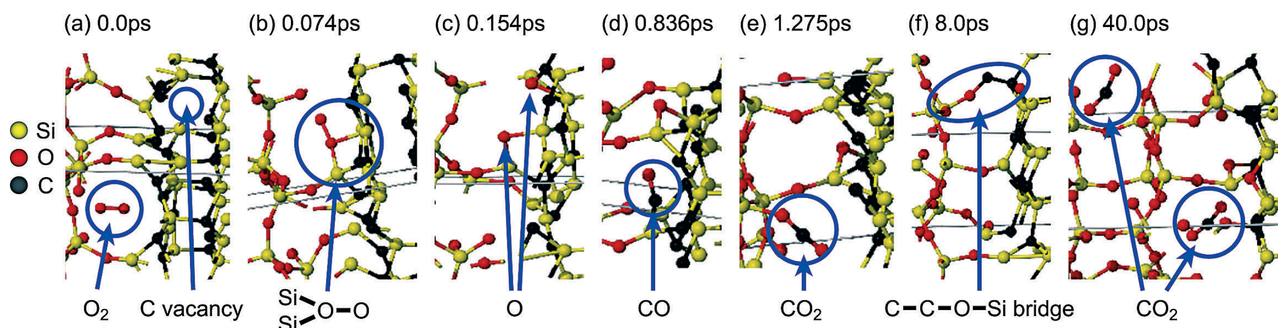

Fig. 5 First-principles molecular dynamics study of SiO_2/4H-SiC(000-1) C-face interface at 2500 K. In this initial interface structure, a silicon vacancy is introduced at the SiO_2/SiC interface. (a) 0 ps (b) 0.074 ps (c) 0.154 ps (d) 0.836 ps (e) 1.275 ps (f) 8 ps (g) 40 ps.

SiCデバイス酸化膜の第一原理分子動力学シミュレーション

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SiCを用いた半導体デバイスは原子炉や宇宙環境等、極限環境下で用いられる素子として期待されている。しかしながら、現状ではSiCの酸化膜とSiCの界面に存在する欠陥がデバイス特性を落としているため、SiCデバイスは期待されたような性能が出せないでいる。実デバイスにおけるSiO_2/SiC界面構造を計算機上で模擬するためには、アモルファスSiO_2/SiC界面構造を構築することが重要になる。アモルファスSiO_2/SiC界面構造を構築するために、第一原理分子動力学コードを用いた加熱・急冷計算を行った。計算の初期構造にはアモルファスSiO_2/SiC界面構造を十分に生成出来るだけの大きさを持ったスラブモデルを用いた。加熱・急冷計算の結果、界面モデルのSiO_2層はアモルファス構造になった。生成された界面モデルは無欠陥構造では無く、界面には5配位のSiを含む欠陥構造が見られた。この5配位欠陥構造は冷却速度を–2000K/psから–500K/psまで遅くすることで消滅した。第一原理分子動力学計算によってSiO_2/4H-SiC (C面) 界面における酸化過程のシミュレーションを行った。分子動力学計算は2500Kで行った。O_2分子は界面のSiO_2層中かSi原子付近で解離した。O_2分子のO原子はSiC界面のC原子を酸化し、Si-C-O複合体を構成した。

キーワード：SiCデバイス, 第一原理計算, 分子動力学, 界面欠陥, 酸化過程