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, SiC devices don't present theoretically expected performance levels. This is considered to be attributed to defect at the SiO_2/SiC interface that degrades the electrical performance of the device. The oxide layer of the real device has an amorphous structure, and there is an interlayer in the SiO_2/SiC interface. To emulate the real device interface structure with the computer simulation, it is important to construct the amorphous SiO_2 structure on SiC. The slab model using 693 atoms for a-SiO_2 on a 4H-SiC(0001) crystal layer was constructed by using first-principles molecular dynamics simulation code optimized for the Earth-Simulator. The heating and quenching method was carried out to make an a-SiO_2/SiC interface structure. The Si-O bond length, the O-Si-O bond angle, and the Si-O-Si bond angle of the SiO_2 layers of the interface structure were 0.165 nm, 109 deg, and 135 deg, respectively. Because these values had been suited for the condition of a-SiO_2, it was confirmed that an excellent a-SiO_2/SiC interface structure had been generated by heating and quenching calculation.

We performed first-principles molecular dynamics simulation of the SiO_2/4H-SiC(0001) interface oxidation process. The O_2 molecules are added one by one every 8ps up to the 10th O_2 molecule in the SiO_2 layer near the interface in the simulation of the oxidation process, and the molecular dynamics calculation was carried out to 74.4ps. The Si layer at the SiC interface is fully oxidized, and has become the SiO_2 layer. We observed the dissociation process of the O_2 molecule and the transition state of the reaction. The C cluster, which is considered one of the candidate structures of the interface traps, is formed in the interface layer.

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 nuclear power plants. The performance of SiC MOSFET devices to date is below theoretically expected performance levels. This is widely considered to be attributed to defect at the SiO_2/SiC interface that degrades the electrical performance of the device. The relation among atomic structures, interface defects and electrical characteristics is not clear at present though many researchers have been studied to solve these problems. In this study, we tried to solve these problems by the computer simulation of electronic structure of the SiO_2/SiC interface. The oxide layer of the real device has an amorphous structure, and there is an interlayer in the SiO_2/SiC interface. To emulate the real device interface structure with the computer simulation, it is important to construct the amorphous SiO_2 (a-SiO_2) structure on SiC. In case of a conventional calculation[1], a-SiO_2/SiC interface structure has been substituted by the crystal SiO_2/crystal SiC structure that can be easily simulated by small-scale calculation. In such a small-scale calculation, a complex SiO_2/SiC interface structure was not able to be simulated because the number of atoms included in these calculations was about 100 atoms at most, and the number of interfacial atoms was about only 6–10. In this study, to simulate interfacial property more precisely, we aimed to generate a-SiO_2/SiC structure with large-scale calculation to which the amorphous structure was able to be constructed. And we carried out the dynamical simulation of the oxidation process for the first-principles molecular dynamics calculation of the SiO_2/SiC interface.

2. Simulation result

2.1 Parameter search in the heating and quenching calculation that uses medium-scale interface model

Amorphous SiO_2/SiC interface structure is made by applying the heating and quenching calculation that uses the

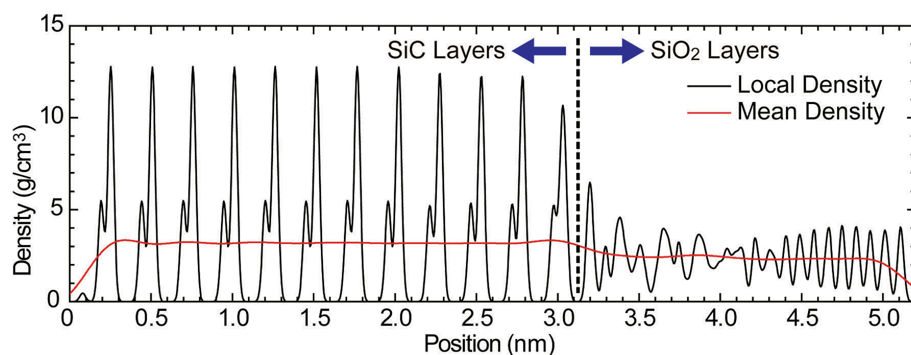

Fig. 1 The atomic density of the 444 atoms of SiO_2/SiC interface structure at room temperature.

first principles molecular dynamics code VASP (Vienna ab-initio Simulation Program)[2–4] to the atomic interface structure model that consists of SiC crystal substrate and crystalline SiO_2 thin layers on the substrate. Various parameters of the generation temperature condition etc. were decided by the trial calculation that used the medium scale model.

The heating and quenching calculation of 444 atoms of SiO_2/SiC interface structure that had been done last year[5] used the condition of 3.0 ps heating by 4000 K and the cooling speed of –1000 K/ps. The SiO_2 surface layer was fixed to prevent the interface atomic structure destruction at the high temperature heating. The Si-O bond length, the Si-O-Si bond angle, and the O-Si-O bond angle of the SiO_2 layers are 0.165 nm, 145 deg, and 107 deg, respectively in interface structure after cooled down to the room temperature. It was confirmed that the values had suited the condition of *a*-SiO_2 structure[6].

The atomic density of the interface structure was obtained in the direction of the perpendicular of the interface. (Fig. 1) The density of the SiC layer shows a periodic change that reflects the crystalline structure. A periodic change was not seen in the density of the SiO_2 layers near the interface; therefore, these layers are good amorphous structures. However, the density of the SiO_2 layers near the surface shows a periodic change, that is the layers looks like the crystal. It is guessed that the recrystallization occurred from the surface by the process of quenching because the crystalline structure remained near the SiO_2 surface that had been fixed in heating until entering the quenching process. It was suggested that the continuance annealing be necessary after the surface had been released. As a result of searching for the annealing condition, all SiO_2 layers become the amorphous structures when the SiO_2 surface is opened at 3500K in the cooling process and SiO_2 layers are continuously annealed for 2ps keeping the temperature.

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

A large-scale interface structure that simulated a real device was generated according to the temperature condition decided by the heating and quenching calculation that used the medium scale interface model. The generation of *a*-SiO_2/SiC interface structure was tried by using the large scale model that consisted of 1017 atoms (693 atoms at the heating and quenching calculation). In the amorphous interface structure generation using the medium-scale model, it was observed that the recrystallization occurred in the quenching process from the SiO_2 surface fixed to the crystalline structure in the quenching process. Then, in the large scale model, it was tried to improve amorphous structure near the surface on the following conditions based on the heating temperature condition in the medium scale model. The interface structure melts by heating on the condition of fixing the surface, and the structure is annealed continuously when it is cooled below the temperature that it doesn't destroy. Figure 2 shows the total energy of the interface structure and the temperature condition of the heating and quenching process. In addition, the figure shows the atomic structure images of the interface model in a typical point. The beta quartz is connected on the Si plane of 4H-SiC(0001) crystal in an initial interface structure. The SiO_2 layers melted heating the structure by 2 ps in the temperature of 4000K on the condition of fixing SiC layers except 2 interfacial layers, surface Si of SiO_2 layers and H that terminate surface Si. The interface structure has been cooled down to the temperature of 3500K without changing the condition of being fixed. After the removal of H that terminated surface Si and release of surface Si, the interface structure was continuously annealed for 2 ps at the temperature of 3500K. After free interfacial SiC layers had been expanded from two layers to four layers, the interface structure was quenched to the room temperature.

The atomic density in the process of heating and quenching was obtained. Figure 3 shows the atomic density in the interface structure in the direction of the perpendicular of the interface. In the initial state of (1), the density of the interface structure shows periodic distribution that reflects the crystalline structure. When the melting process ended at (2), the periodic density distribution of the SiO_2 layer was lost, and the structure became random. The density on the SiO_2 surface

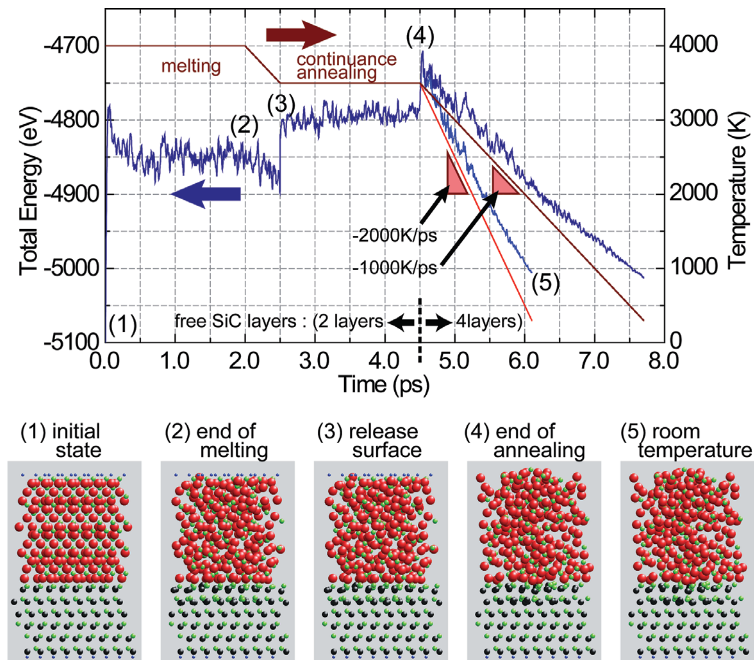

Fig. 2 The total energy of the interface structure, the temperature condition of the heating and quenching process and the atomic structure images of the interface model.

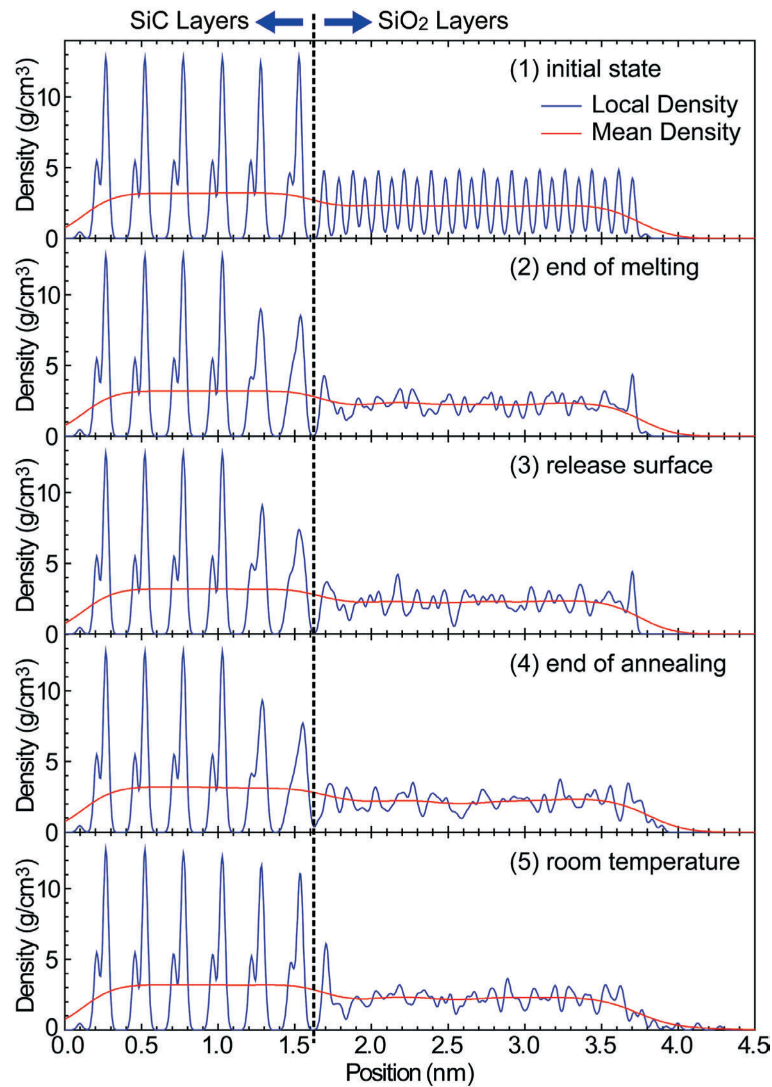

Fig. 3 The atomic density in the interface structure.

had the peak until the surface is released at (3) because Si and H atom in surface had been fixed to the crystal position. All layers of SiO_2 structure became random by the time the continuing annealing ended at (4). It was confirmed that the recrystallization had not occurred because the periodic density structure had not been observed after interface structure had been cooled down to the room temperature at (5).

Figure 4 shows the radial pair distribution function (RDF) of all atoms (total RDF) and partial RDF derived by selecting the distance and existence probability between specific elements of the SiO_2 layers after it cools down to room temperature. It is suggested that all SiO_2 layers are good amorphous structures because fine structure that reflects the long range order is not observed in total RDF. The first peak at 0.165 nm in total RDF originates in the Si-O bond length as a result of evaluating partial RDF. The second peak at 0.268 nm in total RDF originates at the nearest neighbor distance of O and O. Because the O-O bonding doesn't exist in SiO2 layers, this peak originates in O and O distance in the O-Si-O bondings. When 0.165 nm of the Si-O bond length is used, the O-Si-O bond angle becomes 109 deg. It agrees well with the tetrahedral coordination angle of Si. Similarly, the small peak at 0.305 nm in total RDF originates in Si and Si distance of Si-O-Si bondings, and the Si-O-Si bond angle becomes 135 deg. There is a small peak about 0.23 nm in partial RDF of Si and Si. This means the Si-Si bonding actually exists in SiO_2 layers as a defect structure. The short range order of the bond length and the bond angle obtained from the result of the analysis of these partial RDF has suited the condition of a-SiO_2. Therefore, it was confirmed that an excellent a-SiO_2/SiC interface structure was generated by heating and quenching calculation.

When the interfacial atomic structure was analyzed in detail after it was quenched to the room temperature, a lot of defect structures were observed near the interface in addition to the Si-Si bonding to which existence was clarified by the result of the RDF analysis. The Si dangling bond, the Si-Si bonding, and 5 coordinations Si were observed near the interface. In addition to these defects, the O dangling bond and 3 coordinations O were observed in SiO_2 layers. There was no defect in the SiC layers. It is thought that these defects were generated with the following reasons. When the a-SiO_2 and the SiC crystal are connected, significant structure changes such as the losses of the symmetry and density reduction occur in the interface. Especially, O density in the interface rises too much if all interface Si have bonding to O. To relax these distortions near the interface, the defect structure will be introduced. In the future, we will derive the electronic structure of these defect structures, and desire to clarify the relation between the defect structures and the interface states.

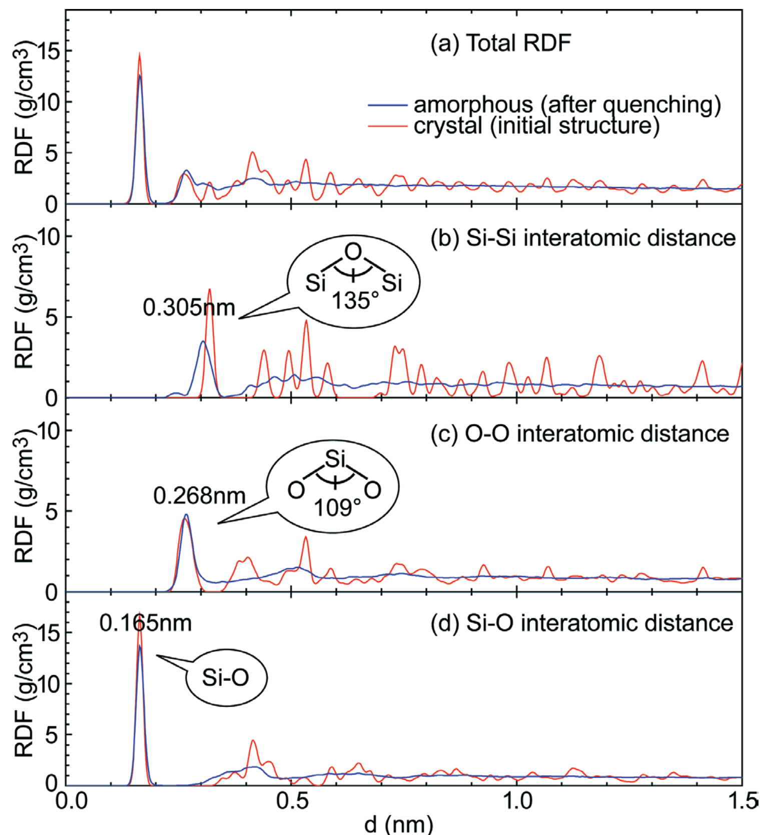

Fig. 4 Total and partial RDF of the SiO_2 layers in the interface structure.
blue line: after quenching structure
red line: reference (initial structure)

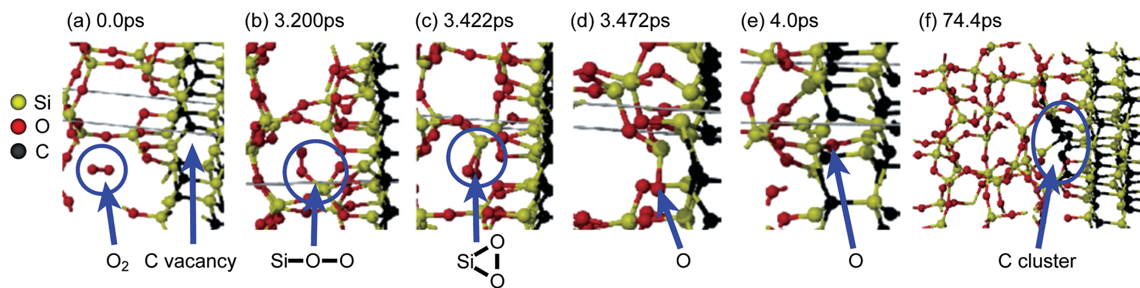

Fig. 5 First-principles molecular dynamics study of the SiO_2/4H-SiC(0001) interface at 2500K. The first O_2 molecular was put at 0ps. (a) 0ps, (b) 3.2ps, (c) 3.422ps, (d) 3.472ps, (e) 4.0ps and (f) 74.4ps.

2.3 Dynamical simulation of SiO_2/SiC interface oxidation process

We performed first-principles molecular dynamics simulation of the SiO_2/4H-SiC(0001) interface oxidation process[5]. In the actual SiO_2/SiC interface, the transition oxide layer is observed, and it contains vacancies and dangling bonds. These defects may be the trigger of oxidation. In order to trigger the oxidation process, the C vacancy is introduced into the SiC layer near the interface. The O_2 molecules are added one by one to the empty sphere in the SiO_2 layer near the interface in the simulation of the oxidation process.

The results of the molecular dynamics calculation of the SiO_2/4H-SiC(0001) interface with the C vacancy are shown in Fig. 5. We put the first O_2 molecule in the empty sphere of the SiO_2 layer. The dissociation of the O_2 molecule occurred as follows. In the fist step, the O_2 molecule is bonded to the Si atom, and the Si atom becomes five coordinates as shown in Fig. 5 (b). In the second step, both O atoms of the O_2 molecules are bonded to the same Si atom and a triangular configuration is formed Si-O-O. In the third step, the bond of the O_2 molecule is broken but both O atoms of the O_2 molecule retain their bonds with the Si atom. The O atom bonded to the Si atom of the SiO_2/SiC interface moves to the C vacancy position in the SiC layer. Subsequently, an O_2 molecule was added every 8ps up to the 10th O_2 molecule, and the molecular dynamics calculation was carried out to 74.4ps. The Si layer at the SiC interface is fully oxidized, and has become the SiO_2 layer. It is shown that the C atoms at the SiC interface gather in one place and a C cluster is formed, as shown in Fig. 5 (f). The SiC interface, except at the C cluster became the SiO_2 layer. The oxidation of the Si atoms in the third layer from the SiC interface begins[7].

3. Conclusion

To emulate the oxide interface of the SiC semiconductor device expected as an electronic device used under the severe environment, the amorphous SiO_2/crystalline SiC interface atomic structure was generated with the computer simulation of the heating and quenching method that used the first-principles molecular dynamics code VASP. When the SiO_2 layers were extracted from the interface structure generated by heating and quenching calculation that uses 693 atoms and the RDF was evaluated, the fine structure that reflected the long range order was not observed. The Si-O bond length, the O-Si-O bond angle, and the Si-O-Si bond angle of the SiO_2 layers were 0.165 nm, 109 deg, and 135 deg, respectively. Because these values had been suited for the condition of a-SiO_2, it was confirmed that an excellent a-SiO_2/SiC interface structure had been generated by heating and quenching calculation. Various defect structures had been observed with the generation of the interface structure. In the future, we will clarify the relation between the defect structures and the interface states.

We performed the dynamical simulation of the SiO_2/4H-SiC(0001) interface oxidation process using first-principles molecular dynamics. We observed the dissociation process of the O_2 molecule and the transition state of the reaction. The C cluster, which is considered one of the candidate structures of the interface traps, is formed in the interface layer.

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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。実際のデバイス酸化膜はアモルファスであり、SiO_2/SiC界面には中間層が存在する。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。そこで、地球シミュレータに最適化した第一原理分子動力学コードを用いた加熱・急冷計算によって、693原子からなるスラブモデルの*a*-SiO_2/SiC界面構造を生成した。その結果、SiO_2領域のSi-O原子間距離は0.165nm、O-Si-O結合角は109°、Si-O-Si結合角は135°となり、良好なアモルファス状態が再現できていることが分かった。

第一原理分子動力学計算によってSiO_2/4H-SiC(0001)界面における酸化過程のシミュレーションを行った。O_2分子を界面近くのSiO_2層に一つずつ10個まで加えていく事で74.4psまでの酸化過程を分子動力学でシミュレーションした。SiCの界面Si層は完全に酸化され、SiO_2層を形成した。O_2分子の解離プロセスと反応の遷移状態を観測した。界面準位の候補の一つと考えられている炭素クラスタ構造が界面に生成することを確かめた。

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