Generation of Amorphous SiO_2/SiC Interface and Dynamical Simulation of Interface Oxidation Process of SiC Device

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Silicon carbide (SiC) semiconductor devices are expected to be used in severe environments such as outer space and nuclear power plants. However, SiC devices don't present the expected performance. This is considered to be attributed to the defects at the interface between SiC and the oxide (SiO_2) layer that reduce electrical characteristics of them. For the application of computer simulation to the realistic interface structures, it is important to construct the structure of amorphous SiO_2 (a-SiO_2) on SiC. The slab model using 444 atoms for a-SiO_2 on a 4H-SiC (0001) crystal layer was constructed by using first-principles molecular dynamics (MD) simulation code optimized for the Earth-Simulator in order to obtain a more realistic structure and electronic geometry of a-SiO_2/4H-SiC interface. The heating and rapid quenching method was carried out to make an a-SiO_2/SiC interface structure. The heating temperature, the heating time or the speed of rapid quenching is 4000 K, 3.0 ps or -1000 K/ps, respectively. As the result, the interatomic distance and the bond angles of SiO_2 layers agreed well with the most probable values in bulk a-SiO_2, and there were no coordination defects in the neighborhood of the SiC substrate. The first-principle molecular dynamics calculation of the oxidation process on the SiO_2/SiC interface succeeded for the first time. The carbon cluster that seems to be one of the causes of the interface trap formation is formed in the process of the oxidation.

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

1. Introduction

Silicon carbide (SiC) semiconductor device has a radiation-tolerant property that is difficult to obtain by usual Si or GaAs semiconductor devices. It is expected to be used in severe environments such as outer space and nuclear power plants. In addition, insulating layer of silicon oxide (SiO_2) is easily obtained with thermal oxidization of SiC. There is an advantage that conventional Si processing technology can be used for the SiC processing unlike other materials. However, SiC devices don't present the expected performance. This is considered to be attributed to the defects at the interface between SiC and the oxide layer that reduce electrical characteristics of them. A basic research that clarifies atomic structure on SiO_2/SiC interface by difference of oxidation method, investigates origin of interfacial defect and ties interfacial defect structure and electric characteristic are indispensable to solve this problem fundamentally. Though many researchers have been studied to solve these problems, the relation among atomic structures, interfacial defects and electrical characteristics is not clear at present. It is difficult to decide the electric charge state of the defect though the structure of an interfacial defect can be identified from the measurement of a physical structure. On the other hand, it is difficult to know a physical structure though it can know the electric charge state of the defect from electric evaluation of characteristics. On the semiconductor device interface, the microscopic electric charge state of the defect decides a macroscopic electric characteristic. In this study, we tried to solve these problems by the computer simulation. For the application of computer simulation to the realistic interface structures, it is important to construct the structure of amorphous SiO_2 (a-SiO_2) on SiC. In case of a conventional calculation[1], it has been substituted by the crystal SiO_2/SiC interface structure that can be easily simulated by small-scale calculation. Because the number of atoms included in these calculations was about 100 atoms at most, and the number of interfacial atoms was about 6-10, a complex SiO_2/SiC interface structure was not able to be simulated. In this study, to

simulate interfacial property more precisely, we aimed to generate a-SiO_2/SiC structure by the calculation using the large-scale model by which the amorphous structure was able to be constructed.

2. Simulation result

2.1 Generation of a-SiO_2/SiC interface

The defect structure of the oxide and the semiconductor interface are important factors to decide the characteristic of the SiC device. The slab model using 444 atoms for a-SiO_2 on a 4H-SiC (0001) crystal layers was constructed by using first-principles molecular dynamics (MD) simulation code in order to obtain a more realistic structure and electronic geometry of a-SiO_2/4H-SiC interface. The calculations have been performed by the Vienna ab-initio simulation package (VASP) on the Earth-Simulator. Prior to the calculation, the supercells of crystalline form of SiO_2 (β-quartz) on a 4H-SiC (0001) crystal layer was employed as an initial simulation structure. The heating and rapid quenching method was carried out to make an a-SiO_2/SiC interface structure. The heating temperature, the heating time or the speed of rapid quenching is 4000 K, 3.0 ps or -1000 K/ps, respectively. In order to preserve the crystalline structure of the 4H-SiC layers, atoms of SiC substrates other than in four interfacial layers have been fixed during the calculation. We also fixed the terminal in the SiO_2 layer and made a sandwich model that was a structure to place a movable layer between fixed layers. It is tried to improve a disorderly interface by melting and rapid quenching this model, therefore it has been understood to be able to generate an amorphous structure without causing the model's destruction even in 4000K. As a result, a more disordered amorphous area was able to be obtained. In addition, in temperature (2200K) to which model doesn't separate because degree of freedom of system decreased, the fixed SiO_2 terminal was opened to make the SiO_2 layer more amorphous. As a result, total energy of the SiO_2/SiC interface system after quenched to the room temperature, that opens the SiO_2 terminal is lower than total energy of the system that fixed the terminal[2], it is able to be confirmed that the system of open terminal is taking a steady atomic structure (Fig. 1).

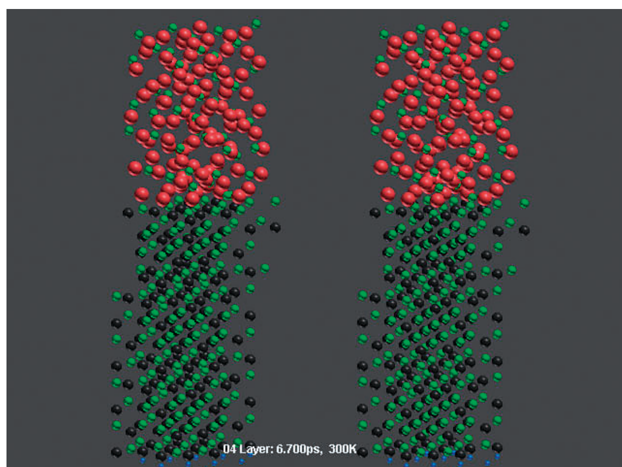

Fig. 1 The atomic structure after quenching to the room temperature using four free layers model (stereograph).

2.2 Radial distribution function and electronic structure of a-SiO_2/SiC interface

The radial distribution function (RDF) of the SiO_2 layers was calculated. Figure 2 shows the RDF change during heating and rapid quenching process. Initial SiO_2 has the β-quartz structure. The long range order of the model was lost at once by heating it by 4000K, and it became a disorderly structure. The variance of the interatomic distance and the bond angle were large though the short range order was kept while heating the model by 4000K. Figure 3 shows the RDF of the layers after quenching to the room temperature. The interatomic distance and the bond angle recovered to a value close to the crystal by the process quenched to the room temperature, and the variance had become small enough, too. The nearest neighbor interatomic distance between Si and O became 0.165 nm. It almost became equal with Si-O bond length of 0.161 nm in the α-quartz. The nearest neighbor interatomic distance between Si and Si became 0.315 nm. When this distance is converted into Si-O-Si bond angle, it becomes 145°. This angle agrees well with 145° ± 10° that is

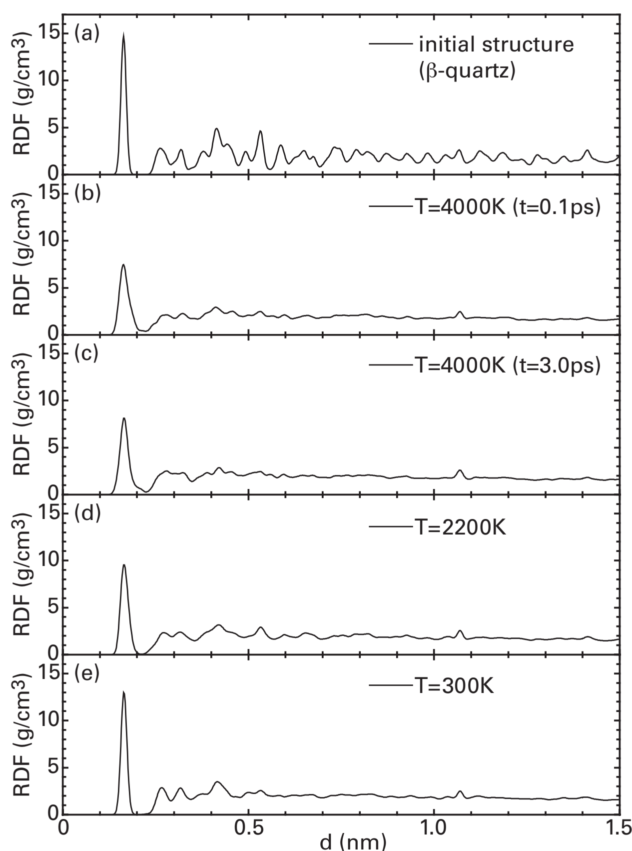

Fig. 2 RDF change during heating and rapid quenching process.

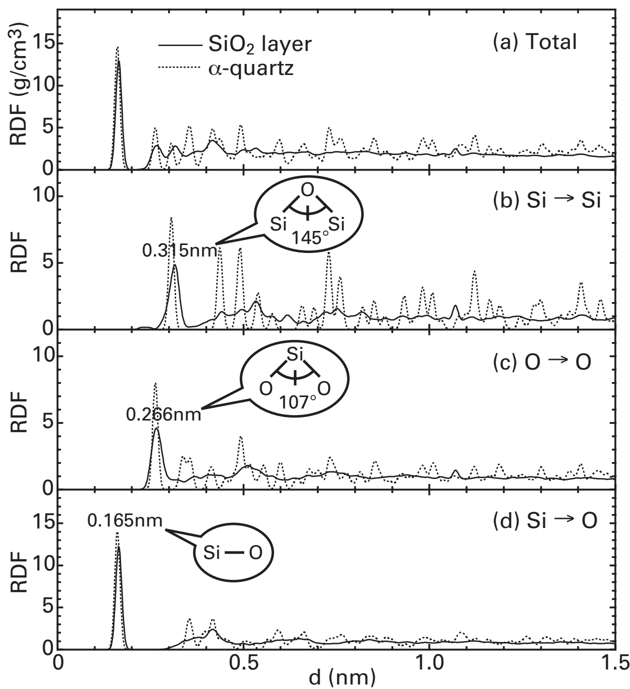

Fig. 3 RDF of the SiO_2 layers after quenching to the room temperature of (a) total atoms, (b) Si to Si atoms, (c) O to O atoms and (d) Si to O atoms (solid). The α-quartz RDF is shown respectively for the reference (dashed).

Si-O-Si bond angle in the silica glass. The nearest neighbor interatomic distance between O and O became 0.266 nm, and is converted into O-Si-O bond angle of 107°. This angle is almost equal to bond angle of 109.5° in Si-atom-centered tetrahedra. While the short range order of the atomic structure recovered the value of the crystal, the degree of disorder in long range still kept large enough to simulate an amorphous structure. Therefore, it was confirmed to be able to generate the a-SiO_2 layer with the simulation of the heating and rapid quenching method.

After quenching to the room temperature, the atomic structure became clean and abrupt a-SiO_2/SiC interface. The coordination defects that existed in every three Si of the neighborhood of substrate in the initial structure disappeared completely. However, a few defects energy levels were still observed by the band gap in density of state (DOS). Two defect energy levels exist from the top of a valence band at the level of about 0.4eV. We examined to which wave function the energy level belonged, and calculated the ratio of the atom that made the wave function. As a result, it was decided that both energy levels were made by almost single atoms. Figure 4 shows the charge density distribution by all electrons and defect energy level, respectively. The defects energy levels are originated from interfacial oxygen. Though this O has bonding with interfacial Si, the other side is not bonded to any atoms, and it becomes a dangling bond. The localized electronic distribution that cannot contribute to bonding causes defect energy levels.

2.3 Simulation of SiC thermal oxidation process

It is important to simulate the thermal oxidation process on the SiO_2/SiC interface dynamically for the clarification of the formation process of the interfacial transition layer that exists on the SiO_2/SiC interface. We simulated the oxidation process on the SiO_2/4H-SiC (0001) interface by the first-principles calculation. The oxidation process was simulated by adding the O_2 molecule to the empty sphere in the SiO_2 layer near the interface one by one, and calculating the first-principles molecular dynamics calculation in 2500K. The number of atoms for each supercell is about 300. The SiO_2/SiC clean and abrupt interface was made by heating and rapid quenching method as well as the preceding section, and this was used as an initial structure of the calculation. In order to be a trigger of the oxidation process, one carbon vacancy is introduced near the interface in SiC layer with the deletion of a carbon from the initial structure. The first O_2 molecule was added to the empty sphere in the SiO_2 layer near the interface. When heating began by 2500 K, the oxygen molecule dissociated, and the oxygen atom moved to

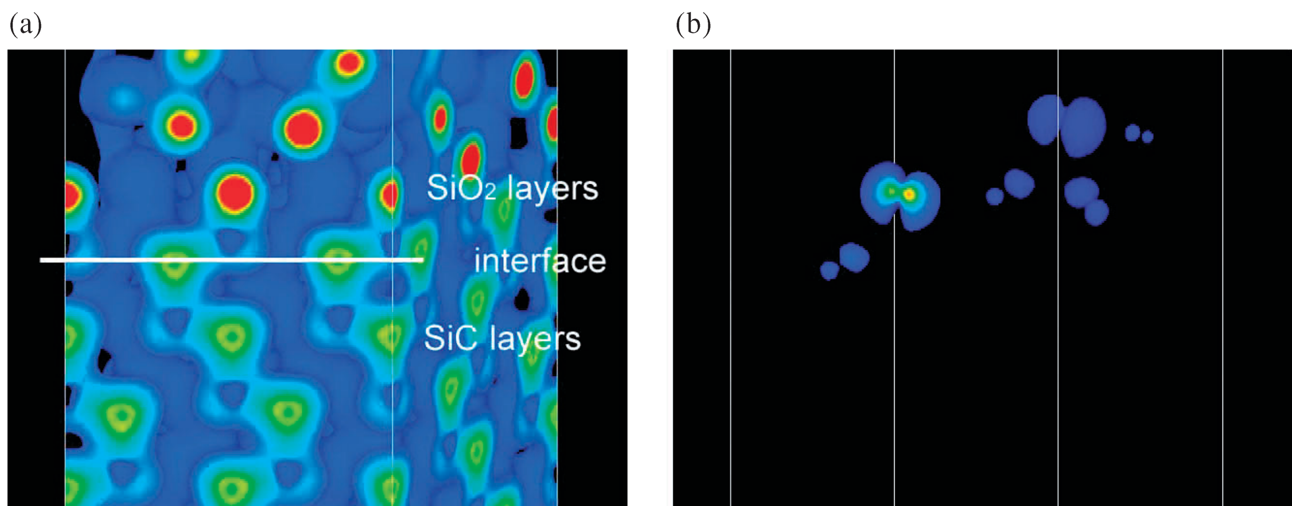

Fig. 4 Charge density distribution of the relaxed terminal model near the interface by (a) all electrons and (b) defect energy level, respectively.

the position of a carbon vacancy after 4.0 ps. At this time, the second O_2 molecule was added to the empty sphere in the SiO_2 layer. After 10.4 ps, the oxygen molecule dissociated, and the second oxygen atom moved to the SiC layer. In addition, the third O_2 molecule was added to the SiO_2 layer. After 18.4 ps, the carbon cluster was formed. The last O_2 molecule was added to the SiO_2 layer. After 23.2 ps, the Si atom in the SiC interface layer was oxidized and it moved to the SiO_2 layer (Fig. 5). It succeeded in a dynamical simulation of the thermal oxidation process on the SiO_2/SiC interface by the first-principles molecular dynamics simulation.

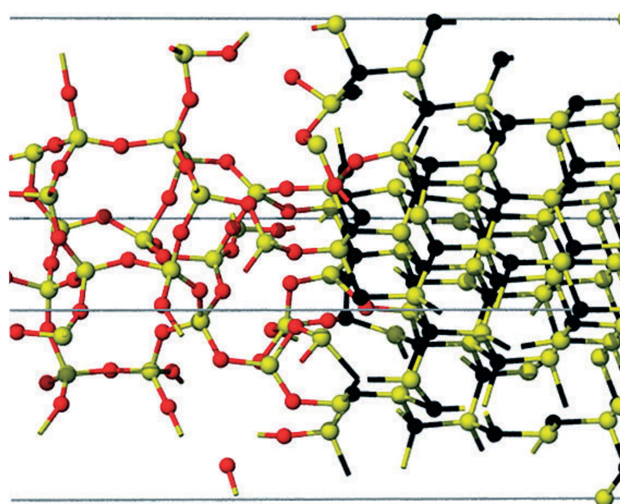

Fig. 5 The atomic structure of SiO_2/SiC interface in the oxidation process after 23.2ps.

3. Conclusion

The slab model using 444 atoms for *a*-SiO_2 on a 4H-SiC (0001) crystal layer was constructed by using first-principles MD simulation. The heating and rapid quenching method was carried out to make an *a*-SiO_2/SiC interface structure. The heating temperature, the heating time or the speed of rapid quenching is 4000 K, 3.0 ps or -1000 K/ps, respectively. In temperature 2200K the SiO_2 terminal was opened to make the SiO_2 layer more amorphous. As the result, the interatomic distance and the bond angles of SiO_2 layers agreed well with the most probable values in bulk *a*-SiO_2. Some energy levels were still observed in the band gap in DOS though there were no coordination defects in the neighborhood of the SiC substrate. The defect energy levels exist from the top of a valence band at the level of about 0.4eV. The localized electronic distribution at the interfacial oxygen that cannot contribute to bonding causes defect energy levels.

The first-principle molecular dynamics simulation of the oxidation process on the SiO_2/SiC(0001) interface succeeded for the first time. The oxygen molecule dissociates in the SiO_2 layer and makes a bonding with the Si atom in SiO_2. The Si atom on the SiC interface moves in the SiO_2 layer by the oxidation. The carbon cluster that seems to be one of the causes of the interface trap formation is formed in the process of the oxidation.

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SiCデバイスにおけるアモルファスSiO_2/SiC界面の生成および酸化過程のシミュレーション

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SiCを用いた半導体デバイスは、従来のSiやGaAs半導体デバイスでは動作が困難な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おり、計算機シミュレーションによってその界面構造を決定し、欠陥構造の原因を探ることが必要である。実際のデバイスにおける界面構造を計算機上で模擬し、欠陥構造がどのようにデバイス特性に影響するのか導出するためには、デバイスでの界面構造を模擬出来るようなアモルファスSiO_2(*a*-SiO_2)/SiC界面構造を計算機上に構築することが重要になる。そこで、地球シミュレータ用に最適化した第一原理分子動力学計算コードを用いて、444原子からなる*a*-SiC/SiO_2界面構造に加熱・急冷計算を行う事でアモルファス構造の生成を行った。加熱温度は4000K、加熱時間は3ps、急冷速度は-1000K/ps、界面でのSiC可動層は4層とし、2200KでSiO_2側終端固定層を開放し自由端とすることによって、SiO_2層でのアモルファス化を促進させた。その結果、SiO_2領域の原子間距離および結合角はバルクの*a*-SiO_2の値と良く一致しており、また、良好なアモルファス状態が再現できていることも分かった。さらに、生成された界面ではダングリングボンドが消滅しており、清浄界面に近い状態が再現されていた。第一原理分子動力学計算によってSiO_2/SiC界面における酸化過程のシミュレーションに初めて成功した。酸化過程の途中で、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