PHYSICAL REVIEW B **79**, 113302 (2009)

Ab initio theoretical study of an oxygen vacancy defect at the 4*H*-SiC(0001)/SiO_2 interface

Eiichi Okuno, Toshio Sakakibara, and Shoichi Onda
Research Laboratory, DENSO CORPORATION, 500-1, Minamiyama, Komenoki-cho, Nisshin, Aichi 470-0111, Japan

Makoto Itoh and Tsuyoshi Uda
AdvanceSoft Corporation, 1-9-20, Akasaka, Minato-ku, Tokyo 107-0052, Japan

(Received 25 November 2008; published 25 March 2009)

In order to study the electronic structures of the SiC/SiO_2 interface, which is made by the oxidation of SiC, we constructed the structural models for the dangling-bond free interfaces of 4*H*-SiC/SiO_2 with the substrate orientations of (0001) and (11$\bar{2}$0). We carried out *ab initio* calculations to find that a stretched oxygen atom appears in the near-interface region of the SiO_2 insulator for the 4*H*-SiC(0001)/SiO_2 interface but not for the 4*H*-SiC(11$\bar{2}$0)/SiO_2 interface. We argue the origin of the experimentally found oxygen vacancy defect near the SiC(0001)/SiO_2 interface.

DOI: 10.1103/PhysRevB.79.113302 PACS number(s): 71.20.Nr, 71.15.Mb

Extensive experimental studies were devoted in the last decade to the development of power electronic devices based on wide band-gap materials. One of such examples is silicon carbide (SiC),[1] for which the large value of the density of interface states (D_{it}) in SiC(0001)/SiO_2 obstacles the development of a SiC-based electronic device.[2] For the origin of the near-interface traps that contribute to D_{it}, two principal candidates have been proposed: one is an intrinsic defect located inside a silicon oxide film and the other is a carbon-related defect at or near the interface.[3–7]

In addition to experiments, there are some theoretical studies on the 4*H*-SiC(0001)/SiO_2 interface[6–11] based on the density-functional theory (DFT) method.[12,13] Since there is the discrepancy in the density of atomic bonds between the bulk SiC and the bulk SiO_2, a simple connection of the two materials, following the method often used in studying the Si/SiO_2 interface,[14] resulted in the creation of the high density of interface states including dangling-bond (DB) states.[8,9] Specifically, these densities become 4.1×10^{-2} Å^{-2} for 4*H*-SiC(0001)/SiO_2 and 3.7×10^{-2} Å^{-2} for 4*H*-SiC(11$\bar{2}$0)/SiO_2, respectively. On the contrary, Knaup *et al.*[6] simulated the oxidation process at high temperatures by the combined use of the classical molecular dynamics and the DFT method.

Here, we take another approach, that is, to connect the bulk SiC and the bulk SiO_2 structures after modifying the atomic structure of the SiO_2 so as to eliminate DB states from an interface. Note that this structural modification is restricted to be in the near-interface region.

Since there are differences in the densities of atoms as well as atomic bonds between the bulk SiC structure and the bulk SiO_2 structure, the emergence of stress, either tensile or compressive, is inevitable. Our aim is to see how the relaxation of the stress proceeds in each case.

In this Brief Report, we use the bulk 4*H*-SiC structure and the α-quartz structure, which are depicted in Figs. 1(a) and 1(b), respectively, as the model systems of the SiC and the SiO_2 and construct the interfaces that connect the bulk structures of these materials. In these figures, C, Si, O, and H atoms are depicted by using the gray, yellow, red, and light gray spheres, respectively.

Since the application of the construction method for the Si(001)/SiO_2 interface models[14] results in the appearance of the DB states at the interfaces due to the difference in the density of the DBs between the bulk 4*H*-SiC structure and the SiO_2 structure,[8,9,15] we devise the alternative method.

First, we pay attention to the fact that SiC is a much

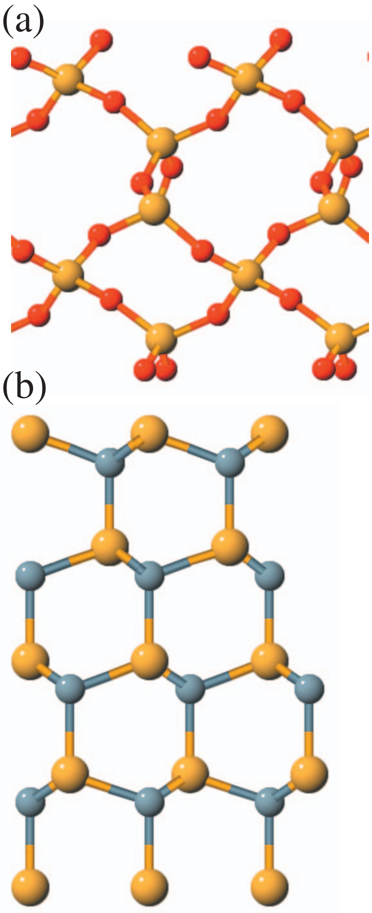

FIG. 1. (Color) The bulk structures of (a) the α-quartz and (b) the 4*H*-SiC. C, Si, and O atoms are depicted by the gray, yellow, and red spheres, respectively.

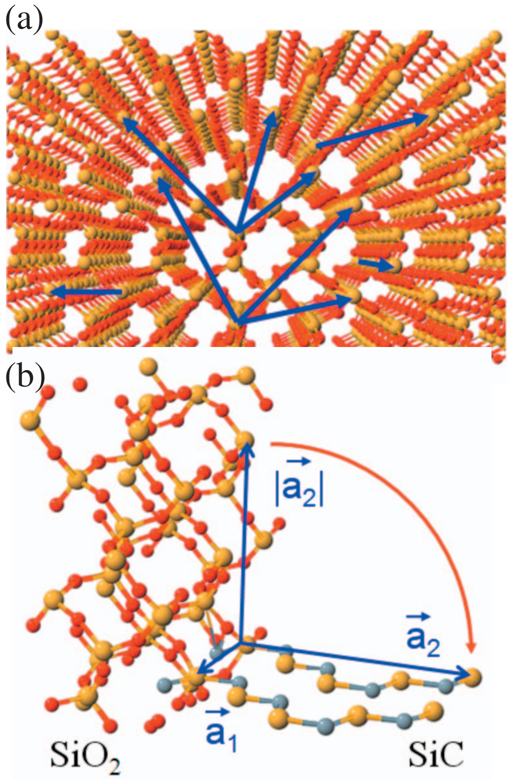

FIG. 2. (Color) (a) The second step in the modeling procedure. To look for a pair of atoms having the distance which approximately coincides with the shorter of the two lattice spacings on the substrate. (b) The third step in the modeling procedure. To rotate SiO_2 until the periodicity of SiO_2 in the a_2 direction approximately coincides with the length of a_2.

harder material with higher density of atomic bonds than SiO_2 is. One method to eliminate DB states from an interface is to adjust the local density of atomic bonds of an silicon oxide near the interface to that of the bulk SiC. Using the α-quartz structure, this is accomplished by the set of the procedures.

(1) Choose the unit cell so that the difference in the number of the DBs between the two systems becomes an even integer.

(2) Choose the direction of the SiO_2 structure, as seen in Fig. 2(a), to let one of its periodicities match the shorter of the two periodicities of the SiC substrate along the interface. We call this direction the a_1 axis hereafter.

(3) Rotate the SiO_2 structure around the a_1 axis until the other periodicity of the SiO_2 structure along the interface matches the longer of those of the substrate, as seen in Fig. 2(b). We call this the a_2 axis and, accordingly, the a_3 axis is taken to be normal to the substrate.

(4) Cut the bottom side of SiO_2 in a curved manner, instead of cutting it along a plane, so as to keep the stoichiometry of the SiO_2 structure. One example is given in Fig. 3(a), in which the section of a curved surface and a plane are depicted by the dotted lines in green and blue, respectively.

(5) Move the atoms at the bottom side of SiO_2 gradually upward so as to increase the local density of atoms near the interface region. At the same time, move these atoms horizontally so as to decrease the horizontal inhomogeneity of the density of atoms near the bottom side. Atoms are moved until the bottom side of SiO_2 becomes nearly flat. See Fig. 3(b).

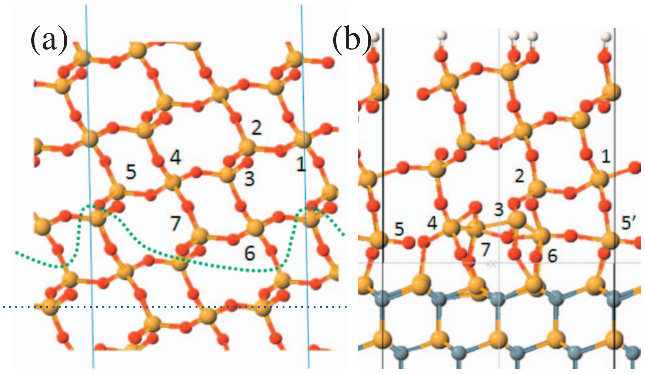

FIG. 3. (Color) (a) One example to eliminate DB states from the interface. C, Si, O, and H atoms are depicted by the gray, yellow, red, and light gray spheres, respectively. Since SiO_2 is inclined in Fig. 3(a), to cut it along a plane may break the stoichiometry (e.g., along the dotted line in blue). Instead, stoichiometry can be retained approximately if the bottom side of the inclined SiO_2 is cut along the dotted curve in green and, afterward, if the silicon atoms numbered six and seven, with the associated oxygen atoms, are pushed upward until (b) the silicon atoms, numbered from three to seven, are nearly aligned to make a pseudoatomic layer. The SiC substrate is also depicted in (b).

(6) Place this locally modified SiO_2 structure on top of the 4*H*-SiC substrate to make the initial atomic structure of an interface.

With these procedures, the difference in the number of the DBs between the SiC substrate and the bottom side of the SiO_2, even if existed, can be resolved if the number of the DB is even. For example, two DBs can be removed with the help of a Si atom having one atomic bond pointing upward and other three bonds downward.[10,11] Hence, the bulk SiC and the bulk SiO_2 can be smoothly connected to each other without creating any coordination defects at the interface. After the initial atomic structure is made by the above method, the structural relaxation calculation is carried out by the DFT method. We will apply these procedures to 4*H*-SiC/SiO_2 with the substrate orientations of (0001) and $(11\bar{2}0)$ and will compare the results.

The calculation conditions are as follows. The DFT calculations are performed within the plane-wave basis set using the DFT calculation software ADVANCE/PHASE.[16] The relaxation calculations are terminated when the maximum force becomes smaller than 0.1 eV/Å. For the pseudopotentials, the Troullier-Martins norm-conserving types[17,18] are used for Si and H atoms, and the Vanderbilt ultrasoft pseudopotentials[19] are used for C and O atoms. The exchange-correlation functional is calculated within the generalized gradient approximation.[20] The wave-function and the charge-density cutoffs are chosen to be 25 and 225 Ry, respectively. The lattice parameters for the bulk 4*H*-SiC structure, we obtained 3.108 and 10.216 Å for the *a* axis and the *c* axis by the calculations, to be compared with the experimental values of 3.073 and 10.051 Å, respectively. In

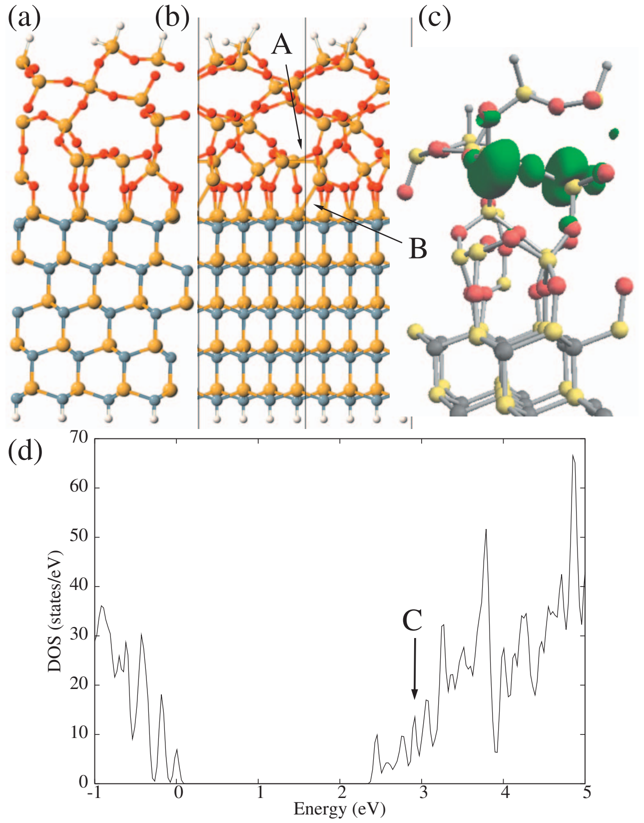

FIG. 4. (Color) (a) The ball-and-stick model of the $4H$-SiC(0001)/SiO$_2$ interface, viewed from the $(1\bar{1}00)$ and (b) the $(11\bar{2}0)$ directions, respectively. The SiC substrate consists of $Si_{40}C_{40}$, whereas the SiO$_2$ part is made of $Si_{14}O_{28}$. Indicated by the arrows and the characters A and B are the direct bonding between two Si atoms. All other atomic bondings are via oxygen atoms. For other explanations, see the caption to Fig. 1. (c) PCD at $E \simeq 2.8$ eV, viewed from the $(11\bar{2}0)$ direction. It is seen that the oxygen atom in the defect is pulled by the Si atoms on both sides. (d) DOS showing the gap states near the conduction-band edge. The correspondence with the PCD in (c) is indicated by the arrow and the character C.

the calculations, the experimental values are used for the lattice parameters in the horizontal directions. In the vertical direction, the vacuum layer with the thickness of larger than 5 Å is used. The DBs at the bottom layer of the SiC substrate and those at the top layer of SiO$_2$ are terminated by H atoms, and all atoms are relaxed by the DFT calculations.

In the structure of $4H$-SiC/SiO$_2$ interface in our previous work[8] although the density of the DB states is more or less similar in the three cases, i.e., SiC(0001)/SiO$_2$, SiC$(000\bar{1})$/SiO$_2$, and SiC$(11\bar{2}0)$/SiO$_2$, the actual number of the DB is one in SiC(0001)/SiO$_2$ and SiC$(000\bar{1})$/SiO$_2$, whereas it is two in SiC$(11\bar{2}0)$/SiO$_2$. This means that the number of the DB states will be two for the SiC(0001)/SiO$_2$ interface if the unit-cell size is made to be twice as large as before. If this is done, two DBs can be eliminated from the interface structures with the help of a Si atom having atomic bonds, one pointing upward and the other three pointing downward.[10,11]

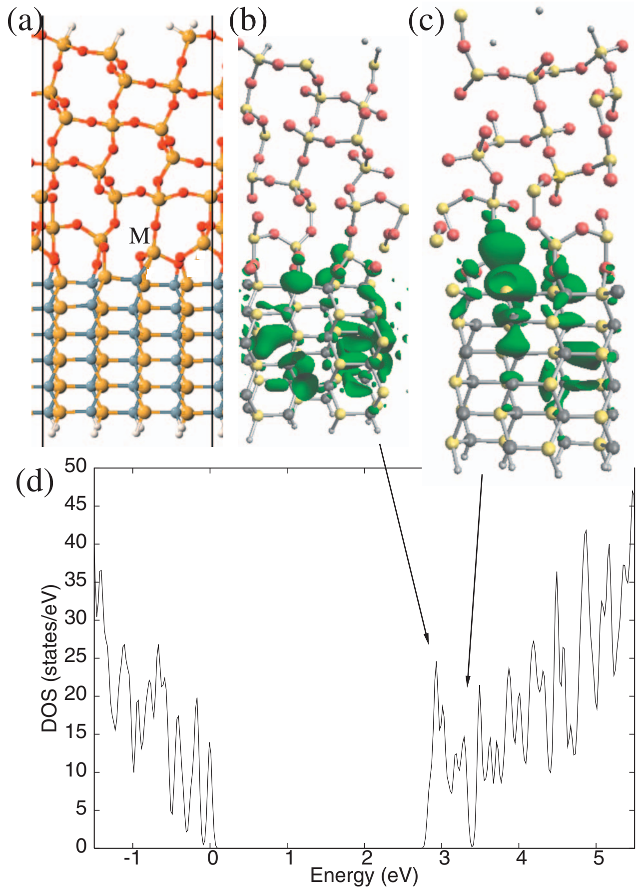

FIG. 5. (Color) (a) The ball-and-stick model of the $4H$-SiC$(11\bar{2}0)$/SiO$_2$ interface. The SiC substrate and the SiO$_2$ structure consist of $Si_{24}C_{24}$ and $Si_{19}O_{39}$, respectively. The vertical lines show the boundaries of the unit cell. For other explanations, see the caption to Fig. 1. The Si atom with symbol M has one upward atomic bond and three downward ones. (b) PCD at $E \simeq 2.9$ eV. (c) PCD at $E \simeq 3.2$ eV. (d) DOS. The correspondence between the peaks in the gap and the PCD's in (b) and (c) are indicated by the arrows.

We first apply this construction procedure to the $4H$-SiC(0001)/SiO$_2$ interface. The relaxed atomic structure and its density of states (DOS) are seen in Figs. 4(a) and 4(b), respectively. In Fig. 4(a), the a_1 axis, the a_2 axis, and the a_3 axis are in the directions of $[1\bar{1}00]$, $[11\bar{2}0]$, and $[0001]$, respectively. There are direct bonding between Si atoms, as indicated by the symbols, A and B. Between them, the latter arose due to the presence of the Si atom which has one atomic bond pointing upward and other three bonds downward. Figures 4(b) and 4(c) show that one of the oxygen atoms inside the SiO$_2$ structure is pulled by the Si atom on both ends to result in the appearance of the electronic states near the conduction-band edge in Fig. 4(d).[21] This defect structure is located to be away from the interface by about 5 Å.[22]

The appearance of this defect can be understood as the consequence of the areal density of atomic bonds across a plane parallel to the interface decreases rapidly from SiC to SiO$_2$ as the distance from the interface d increases. Hence, the tensile force exerts to the atoms inside SiO$_2$ and the atomic bonds of the oxygen atom become nearly straight at $d \simeq 5$ Å. The cross section of the electronic structure is shown in Fig. 4(c), in which we can see that the sp^3 rehybridization of the atomic orbitals for the Si atoms on the both ends of the stretched oxygen atom is broken. We checked this result by using a thicker layer of SiO_2 and found that this defect structure does not disappear.

These results suggest that the oxygen vacancy, which is often observed experimentally near the SiC(0001)/SiO_2 interface,[3] may be caused by the stress induced by the rapid decrease in the areal density of atomic bonds from SiC to SiO_2 as measured across the planes parallel to the interface.

Unlikely to the above case, when we applied the same procedures to the interface structure of $4H$-SiC$(11\bar{2}0)$/SiO_2, we found no intrinsic defect structures inside SiO_2. This difference originates from the fact that the areal densities of the DB states without the structural modification for the SiO_2 structure is larger for $4H$-SiC(0001)/SiO_2 than $4H$-SiC$(11\bar{2}0)$/SiO_2, as we wrote before.

The relaxed atomic structure and its DOS for the $4H$-SiC$(11\bar{2}0)$/SiO_2 interface are seen in Figs. 5(a) and 5(b), respectively. In Fig. 5(a), the a_1 axis, the a_2 axis, and the a_3 axis are taken to be in the directions of $[1\bar{1}00]$, [0001], and $[11\bar{2}0]$, respectively. The Si atom with one atomic bond pointing upward and other three bonds downward is indicated with the symbol M in Fig. 5(a). Figures 5(b) and 5(c) show that the electronic defect structures reside at the interface and inside SiC but not anywhere in the SiO_2 structure. Indicated with arrows in Fig. 5(d) are the partial charge densities (PCDs) at the energy levels of $E=2.9$ eV and $E=3.2$ eV, to be compared with the charge distributions in Figs. 5(b) and 5(c), respectively. It is seen in Fig. 5(d) that the stress induced at the interface spreads into the SiC$(11\bar{2}0)$ substrate because, as seen in Fig. 5(a), atoms in the SiC substrate are tightly connected to each other to form the bilayer structure.

In summary, we showed by the theoretical calculations that the rapid decrease in the areal density of atomic bonds from SiC to SiO_2 causes the tensile stress and the stretched oxygen atom appears in the near-interface region of SiO_2 for SiC(0001)/SiO_2. In the high-temperature oxidation process, this may result in the occurrence of the oxygen vacancy defect.

For the SiC$(11\bar{2}0)$/SiO_2 interface, on the contrary, stress effect is found to spread inside the SiC substrate along the bilayer structure. Our results can be tested experimentally by examining whether the defect structure we argued can be found at the $4H$-SiC$(11\bar{2}0)$/SiO_2 interface and also by measuring the azimuthal dependence of the mobility for the electron carrier transport and D_{it} of the $4H$-SiC$(11\bar{2}0)$/SiO_2 interface on the orientation of the SiC$(11\bar{2}0)$ substrate.

---

[1] *Silicon Carbide*, Optoelectronic Properties of Semiconductors and Materials, edited by Z. C. Feng and J. H. Zhao (Taylor & Francis, New York, 2003).

[2] N. S. Saks, M. G. Ancona, and R. W. Rendell, Appl. Phys. Lett. **80**, 3219 (2002).

[3] V. V. Afanasev, M. Bassler, G. Pensl, and M. Schulz, Phys. Status Solidi A **162**, 321 (1997).

[4] J. L. Cantin, H. J. von Bardeleben, Y. Shishkin, Y. Ke, R. P. Devaty, and W. J. Choyke, Phys. Rev. Lett. **92**, 015502 (2004).

[5] S. Wang, S. Dhar, S. R. Wang, A. C. Ahyi, A. Franceschetti, J. R. Williams, L. C. Feldman, and S. T. Pantelides, Phys. Rev. Lett. **98**, 026101 (2007).

[6] J. M. Knaup, P. Deak, T. Frauenheim, A. Gali, Z. Hajnal, and W. J. Choyke, Phys. Rev. B **71**, 235321 (2005).

[7] J. M. Knaup, P. Deak, T. Frauenheim, A. Gali, Z. Hajnal, and W. J. Choyke, Phys. Rev. B **72**, 115323 (2005).

[8] E. Okuno, T. Sakakibara, S. Onda, M. Itoh, and T. Uda, Jpn. J. Appl. Phys. **1**, 061401 (2008).

[9] T. Ohnuma, H. Tsuchida, and T. Jikimoto, Mater. Sci. Forum **457–460**, 1297 (2004).

[10] F. Devynck, F. Giustino, and A. Pasquarello, Microelectron. Eng. **80**, 38 (2005).

[11] F. Devynck, F. Giustino, P. Broqvist, and A. Pasquarello, Phys. Rev. B **76**, 075351 (2007).

[12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[13] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[14] T. Yamasaki, C. Kaneta, T. Uchiyama, T. Uda, and K. Terakura, Phys. Rev. B **63**, 115314 (2001).

[15] T. Ohnuma, H. Tsuchida, T. Jikimoto, A. Miyashita, and M. Yoshikawa, Mater. Sci. Forum **483-485**, 573 (2005).

[16] The URL address is http://www.advancesoft.jp/product/advance_phase/

[17] N. Troullier and J. L. Martins, Solid State Commun. **74**, 613 (1990).

[18] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[19] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[20] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[21] DFT method gives a band gap which is often smaller than the experimental value. See also http://en.wikipedia.org/wiki/Band_structure

[22] A similar result was obtained for the $4H$-SiC$(000\bar{1})$/SiO_2 interface.