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Ab initio calculations of the β-SiC(001)/Ti interface

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Ab initio pseudopotential calculations of the β-SiC(001)/Ti interface have been performed, and are compared with our preceding results of the SiC(001)/Al interface [Phys. Rev. B **57**, 2334 (1998)]. The C-terminated and Si-terminated interfaces have quite different features, similarly to the SiC(001)/Al interface. For the Si-terminated interface, the Si-Ti bond has a metallic character similar to the Si-terminated SiC/Al interface. For the C-terminated interface, the C-Ti bond has strong p-$d\sigma$ covalent interactions between C $2p$ and Ti $3d$ oribitals like bulk TiC. The C-Ti bond length is very small like bulk TiC although the back Ti-Ti bond is greatly weakened. The adhesive energy of this interface is much larger than the other SiC/Ti and SiC/Al interfaces. It can be said that for the C-terminated interface, a solid-state reaction can occur even at low temperature only at the interface layers, which is in good agreement with experiments. For the Schottky-barrier height, the difference between the C-terminated and Si-terminated interfaces has a similar tendency to the SiC/Al interface, which can be explained by the difference in the interface dipole.

I. INTRODUCTION

SiC is very important materials for high-temperature, high-speed, and high-power electronic and optoelectronic devices as well as high-temperature structural ceramics. It is crucial for such electronic and structural applications to fabricate SiC/metal interfaces[1] with desirable electronic, mechanical, and thermal properties. A large number of experiments have been performed for the SiC/Ti system, because Ti or Ti-containing alloys are often used for such applications. In SiC brazing by Ti-containing molten alloys,[2,3] TiC layers are preferentially formed at the interface, and Si atoms from the dissociation of SiC seem to diffuse into alloys. In solid-state reactions of SiC surfaces with deposited Ti in ultra-high vacuum,[4,5] a layer of TiC is also preferentially formed at the interface, and Si atoms seem to diffuse through the TiC and subsequently form Ti silicides such as Ti_5Si_3 in high-temperature annealing. High-resolution transmission electron microscopy observations[2,3,6] have shown that SiC/TiC interfaces have lattice-matched epitaxial configurations such as α-SiC(0001)/TiC(111) or β-SiC(111)/TiC(111).

For the initial stage of interface reactions, it has been observed that C atoms at SiC surfaces have strong reactivity with Ti even at low temperature. Bellina and Zeller[4] have shown through Auger electron spectroscopy (AES) that excess surface C atoms at C-rich β-SiC(001) surfaces react with deposited Ti and form TiC at least less than 300 °C. By high-temperature annealing, Ti attacks the SiC substrate after consuming excess C. Hasegawa and coworkers[7] has investigated the behavior of the β-SiC(001) $c(2\times2)$ surface, namely the C-terminated (001) surface,[8] upon room temperature deposition of Ti using AES and low-energy electron diffraction (LEED). Results indicate that only the surface C atoms react with Ti without breaking back Si-C bonds at room temperature. As for the reactivity of the Si-terminated surface, Porter and coworkers[5] have observed that a nearly coherent SiC(0001)/Ti interface without any reaction layers can be formed by room temperature deposition of Ti on the Si-terminated 6H-SiC(0001) surface. There are no x-ray photoelectron spectroscopy (XPS) signals for Ti-silicide formation, although the XPS indicates the partial presence of the Ti-C bonds.

On the theoretical side, *ab initio* calculations of the atomic and electronic structure of the SiC(111)/TiC interface[9] has been performed using the full-potential linear-muffin-tin orbital method based on the local density-functional theory (LDFT).[10] However, it is of great importance to clarify the nature of direct interfaces between SiC and Ti before generating compound layers in order to understand the interface reactions. It is of much interest to understand different reactivity of C and Si atoms at SiC surfaces with Ti mentioned above. For this problem, only semiempirical molecular-orbital calculations[11] have been performed. In this paper, we perform *ab initio* calculations of the SiC(001)/Ti interface. We deal with both C-terminated and Si-terminated (001) interfaces in order to examine the C-Ti and Si-Ti interactions, respectively. We use an *ab initio* pseudopotential method, and obtain stable atomic configurations at zero temperature, adhesive energies and electronic properties of the two interfaces. In addition, the present results are compared with our preceding calculations[12] of the C-terminated and Si-terminated SiC(001)/Al interfaces.

By the way, we emphasize the importance of the study of the SiC/Ti system in the field of basic studies of ceramic/metal interfaces.[13–15] From studies using recent electron microscopy techniques and theoretical calculations,[12–21] it can be generally said that the bonding nature and adhesion of ceramic/metal interfaces are dominated by the following two factors. The first factor is the combination of the bonding nature of respective ceramics and metals. The second factor

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is the problem of polar interfaces, termination atoms, or interface stoichiometry. As for the first factor, interfaces between ionic solids and noble or simple metals such as MgO/Ag or MgO/Al systems are often non-reactive experimentally. *Ab initio* calculations of such interfaces[16,17] have shown that the adhesion is explained mainly by electrostatic effects, which partially justify the classical image interaction model.[18] However, if metals are transition metals with reactive *d* orbitals, there should exist covalent interactions such as p-d hybridization as predicted by *ab initio* calculations of the MgO(001)/Ti (Ref. 19) and $Al_2O_3(0001)$/Nb interfaces.[20] On the other hand, interfaces between covalent solids and metals are often seen to be reactive experimentally, where strong interactions such as orbital hybridization and charge transfer dominate the adhesion. Our calculations of the SiC(001)/metal interfaces are the first *ab initio* study of such reactive interfaces. Results of the SiC(001)/Al interface[12] have shown that such strong interactions indeed dominate and that the adhesive energy is much larger than nonreactive interfaces. The present examination of the SiC/Ti interface should clarify the effects of metal species.

The second factor, namely the problem of polar interfaces, termination atoms, or interface stoichiometry, has been observed in *ab initio* calculations of the MgO/Cu (Ref. 21) and $Al_2O_3(0001)$/Nb interfaces,[20] where polar and nonpolar MgO surfaces or O-terminated and Al-terminated Al_2O_3 surfaces generate interfaces with quite different features, respectively. For the SiC(001)/Al interface,[12] we have also found that the C-terminated and Si-terminated interfaces have quite different features such as atomic configurations, bond adhesion, bonding nature and Schottky-barrier height (SBH). The same problem is examined for the SiC/Ti interface.

The SBH[22] is one of the most important properties of ceramic/metal or semiconductor/metal interfaces. Currently, it is possible to estimate the SBH at coherent interfaces through supercell calculations based on the LDFT, as performed for $NiSi_2(111)$/Si,[23,24] GaAs(110)/metal,[25] and SiC(111)/TiC interfaces.[9] The comparison of such theoretical results with experiments and with traditional models[22] for SBH should provide insight into the true mechanism of the SBH. In our calculations of the SiC(001)/Al interface,[12] the SBH for the C-terminated interface is quite different from that for the Si-terminated one. This can be understood from the different dipole caused by the different interface charge distribution. However, this is contrary to the traditional models that deny the dependence of the SBH on interface structure.[22] In this paper, we also examine the SBH for each SiC/Ti interface, and discuss the mechanism of the SBH.

II. THEORETICAL METHOD

The details of the computational scheme are given in our preceding paper.[12] Total energies, stable configurations and electronic properties are given in the framework of the *ab initio* pseudopotential method based on the LDFT.[10,26] The electronic ground state is efficiently obtained using the conjugate-gradient technique[27] for metallic systems with an effective mixing scheme[28] preventing the charge sloshing instability.[29] Stable configurations are obtained through relaxation according to Hellmann-Feynman forces.

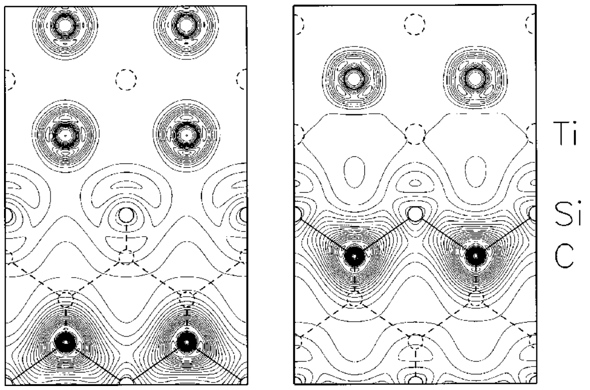

FIG. 1. Relaxed configuration and valence charge density of the Si-terminated SiC(001)/Ti interface. (110) and (110) cross sections are shown. Atoms and Si-C bonds are represented by circles and straight lines. Broken circles and lines represent those not located on the same plane. Contours of the valence electron density are plotted from 0.001 a.u.$^{-3}$ to 0.286 a.u.$^{-3}$ in spacing of 0.015 a.u.$^{-3}$.

We use the TM-type optimized pseudopotentials.[30] For the pseudopotential generation, the configurations $3s^2 3p^{0.5} 3d^{0.5}$ for Si and $2s^2 2p^2$ for C are used. The cutoff radii are 1.8 a.u. for *s*, *p* and *d* orbitals of Si, and 1.44 a.u. for *s* and *p* orbitals of C. For Ti, the configuration $4s^2 4p^0 3d^2$ is used. The cutoff radii are 2.45, 2.55, and 2.25 a.u. for *s*, *p*, and *d* orbitals, respectively. The separable form[31] is used with the local *p* component for Si and C and with the local *s* component for Ti. The plane-wave cutoff energy of 50 Ry is used. The equilibrium lattice constant of SiC is 8.181 a.u., which is about 99.3% of the experimental value.

Each supercell contains a slab of 9 SiC(001) atomic layers, where both surfaces are terminated by the same species. Two sets of five Ti(001) layers are stacked on both surfaces. Fcc Ti is dealt with, although hcp Ti is the most stable. Two free metal surfaces are separated by a vacuum region of about 15 a.u. in the supercell, which ensures stable interlayer distances without any constraint. Coherent interfaces with ideal (1×1) periodicity are dealt with, where Ti layers are expanded along the interface by about 6%. To determine the lowest energy position of the Ti layers parallel to the interface, we examined four special translations[12] corresponding to energy extrema. All the configurations have special symmetry of the point group D_{2d}. Ten special **k** points[32] per irreducible 16th of the Brillouine zone are used. For fractional occupancies, we use the Gaussian broadening scheme[33] with σ=0.2 eV.

III. RESULTS AND DISCUSSION

A. The Si-terminated interface

Figure 1 shows the stable atomic configuration and valence charge distribution on two cross sections. The interface Si atom is fourfold coordinated, and neighbors two Ti atoms. The interlayer distance between the Si and Ti layers is 3.81 a.u., and the Si-Ti bond length is 4.79 a.u. These are much larger than those of the C-terminated interface mentioned below. The Si-Ti bond length is larger than the average of the equilibrium Si-C and Ti-Ti bond lengths, 4.49 a.u.

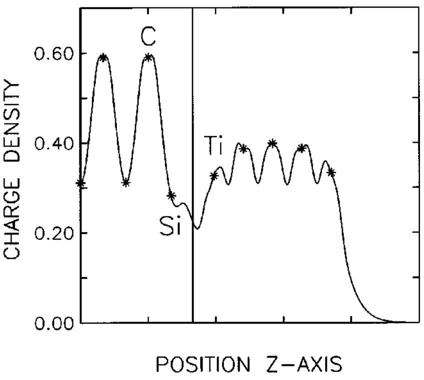

FIG. 2. Valence charge density distribution along the ⟨001⟩ axis of the Si-terminated SiC(001)/Ti interface. Valence charge density is averaged on each (001) plane. The half of the supercell containing 5 SiC and 5 Ti atomic layers with a vacuum region is shown. Asterisks indicate the positions of atomic layers. The interface is marked by a vertical line.

The valence electron density at the interface is relatively small, and is rather broadly distributed. However, the density has a peak above the interface Si atom and *d* electrons are distributed only near Ti atoms. The *d* electrons at the interface Ti atom reveal a slightly polarized distribution different from other Ti atoms. However, there seems to exist no strong hybridization between orbitals of Si and Ti.

Figure 2 shows the averaged charge density on each (001) plane plotted along the ⟨001⟩ axis. At the interface, there exists a charge depletion region near the interface Ti atom, and a small peak near the Si atom as observed in Fig. 1. From Figs. 1 and 2, it can be seen that the atomic configuration and electron distribution recover the bulk features quickly at the back Si-C and back Ti-Ti bonds, although the distribution of *d* electrons at the Ti atoms reveal slight effects of the surface and interface even at the second layers.

The atomic configuration is rather similar to the Si-terminated SiC(001)/Al interface, where the interface Si atom is fourfold coordinated, and the Si-Al bond length is 4.72 a.u. The features of the charge distribution are also similar to those of the SiC/Al interface, although the charge distribution near Ti atoms is different from that near Al atoms, and the peak value of the valence density above the Si atom is larger in the present interface. It seems that the interfacial Si-Ti bond has a rather metallic character similar to the Si-Al bond.

Figure 3 shows the local density of states (LDOS) of the Si-terminated SiC/Ti interface. The LDOS is calculated for each region between successive (001) layers of the supercell.[12] The LDOS at the interface has features like superposition of the Si-partial DOS of SiC and the Ti bulk DOS. This also indicates the rather metallic character of the Si-Ti bond. The LDOS recovers the bulk features at the back C-Si bond and at the back Ti-Ti bond, which is consistent with the features of charge distribution and atomic configuration. However, the peak of the metal-induced gap states (MIGS's) near the SiC valence-band top is attenuated rather slowly inside the SiC. This peak has features of occupied Si dangling-bond states, although there exists some hybridization with Ti 3*d* orbitals.

All the results indicate the rather metallic character of the Si-Ti bond without strong covalent or ionic interactions, similar to the Si-Al bond at the Si-terminated SiC/Al interface. This feature is consistent with the experiments.[5]

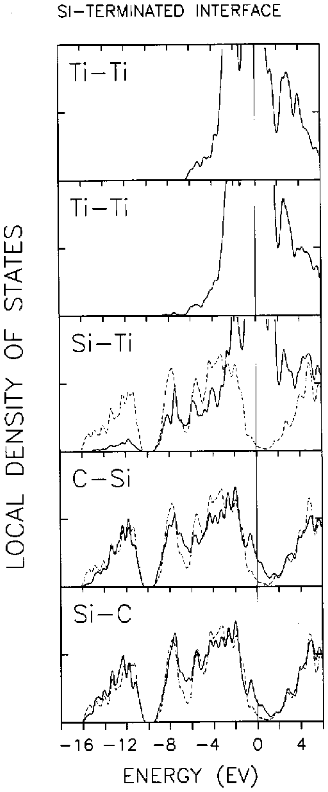

FIG. 3. Local density of states of the Si-terminated SiC(001)/Ti interface. Eigen states for 25 **k** points in the irreducible part are broadened with a Gaussian half width of 0.16 eV. LDOS is given for each region between successive (001) atomic layers. Broken lines represent the LDOS of the central SiC region of the supercell. The Fermi level is indicated by a vertical line.

B. The C-terminated interface

Figure 4 shows the stable atomic configuration and valence charge distribution of the C-terminated interface. Figure 5 shows the averaged charge density on each (001) plane plotted along the ⟨001⟩ axis. Both figures show that the present C-terminated SiC/Ti interface has special features

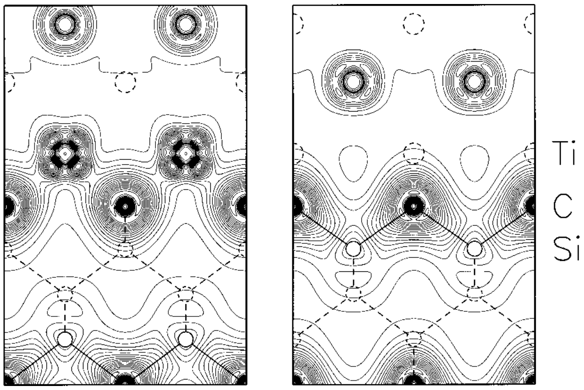

FIG. 4. Relaxed configuration and valence charge density of the C-terminated SiC(001)/Ti interface. Contours of the valence electron density are plotted from 0.001 a.u.^{-3} to 0.271 a.u.^{-3} in spacing of 0.015 a.u.^{-3}.

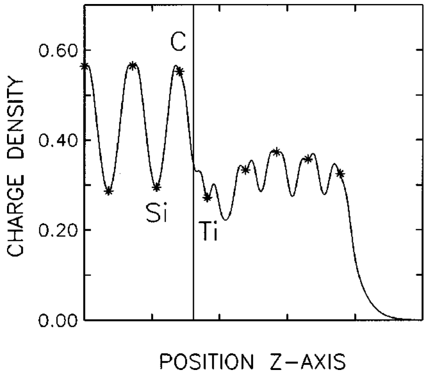

FIG. 5. Valence charge density distribution along the ⟨001⟩ axis of the C-terminated SiC(001)/Ti interface.

quite different from the other SiC/Ti and SiC/Al interfaces. The interface C atom is fourfold coordinated, and neighbors two Ti atoms. The interlayer distance between the C and Ti layers is 2.51 a.u., and the C-Ti bond length is 3.83 a.u. These are much smaller than those of the Si-terminated SiC/Ti interface, 3.81 a.u. and 4.79 a.u., although the C-Ti bond length is larger than the C-Al bond length, 3.51 a.u., in the C-terminated SiC/Al interface. The interlayer distance between the C and Ti layers is smaller than the average Ti-Ti interlayer distance. The opposite is true for the Si-terminated interface.

As for the charge distribution, it is clear that the *d* electrons at the interface Ti atom have special hybridization quite different from *d* electrons of other Ti atoms. The density of the *d* electrons at the interface Ti atom has four humps, and the two humps are directed toward the neighboring C atoms. The electron density of the neighboring C atoms is also increased near the Ti atoms. It should be noted that such charge distribution of the interfacial C and Ti layers is quite similar to that of bulk TiC studied by *ab initio* calculations.[34–36] Ti *d* orbitals in TiC, TiN, and TiO in the NaCl structure are split into e_g-type and t_{2g}-type orbitals in the octahedral crystal field. In TiC, strong $p\text{-}d\sigma$ covalent bonds are formed between C $2p$ orbitals and Ti $3d$ e_g-type orbitals, although the t_{2g}-type component dominates in TiN. In the valence charge density on the (100) plane of bulk TiC,[34,36] the four humps at the Ti atom directed to neighboring C atoms are typical of the dominant e_g component, which is similar to the present charge distribution in Fig. 4. In the present configuration, the interfacial Ti atom is not located in the octahedral environment with equivalent six neighbors, but has two neighboring C atoms and four neighboring Ti atoms. However, the local zigzag chain of the interfacial C and Ti atoms on the (110) plane shown in Fig. 4(a) is common to the local configuration in bulk TiC. The present C-Ti bond length is slightly smaller than the experimental value in bulk TiC, 4.08 a.u. It can be said that the C-Ti bonds with strong $p\text{-}d\sigma$ covalent interactions similar to bulk TiC are formed at the interface.

In Fig. 5, the charge density at the C-Ti bond indicates a partial ionic character also similar to bulk TiC. The valence charge density at the interface C atom is only a little smaller than the bulk value in spite of the lack of two neighboring Si atoms. On the other hand, the charge density at the interface Ti atom is substantially reduced as compared with metallic Ti. This means that electrons of the interface Ti atom are partially transferred toward the C atoms as electrons in bulk TiC. This kind of interfacial charge transfer is observed also in the C-terminated SiC/Al interface.

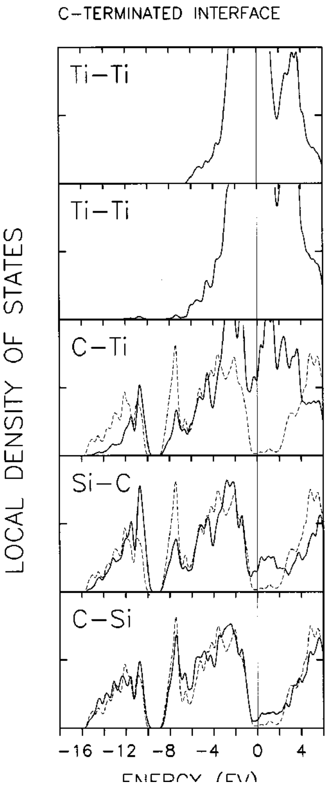

FIG. 6. Local density of states of the C-terminated SiC(001)/Ti interface.

The formation of the strong C-Ti interfacial bond weakens the back Ti-Ti bond. As shown in Fig. 5, the interlayer distance at the back Ti-Ti bond is greatly enlarged by 21.3% as compared with the averaged value, and the valence charge density at the back Ti-Ti bond is greatly reduced. This point is quite different from the other SiC/Ti and SiC/Al interfaces, where the bulk metallic features are recovered quickly at the back metal-metal bonds. Thus it can be said that the interface C and Ti layers are some kind of TiC compounds different from bulk Ti and SiC, and that the back Ti-Ti region with reduced charge density should be regarded as a new interface between TiC and Ti. If we were to perform a tensile test, this new interface should be broken first.

The formation of the strong C-Ti bonds has also large effects on the SiC layers. The 9 SiC(001) atomic layers of the supercell are expanded slightly along the ⟨001⟩ direction. The deviations of the respective (001) interlayer distances from the central C layer to the interface C layer are +5.5%, +4.7%, +4.7%, and −0.2%. The total size of the SiC(001) slab is expanded by 3.7% along the ⟨001⟩ direction. In the Si-terminated interface, the absolute deviations are all less than 1.4%. The present expansion causes a slight reduction in the values of the valence charge density in the SiC region as shown in Fig. 5. The reason of this expansion is not clear. In any case, the formation of the strong C-Ti bonds induces large distortions on both SiC and Ti sides.

Figure 6 shows the LDOS of the C-terminated SiC/Ti interface. The LDOS at the interface also indicates the strong

TABLE I. Calculated bond adhesion of the Si-terminated and C-terminated SiC(001)/Ti interfaces. Results of the SiC(001)/Al interface (Ref. 12) are also listed.

SiC(001)/Ti interface	
Si-terminated	2.52 Jm^{-2}
C-terminated	8.74 Jm^{-2}
SiC(001)/Al interface	
Si-terminated	3.74 Jm^{-2}
C-terminated	6.42 Jm^{-2}

TABLE II. Calculated *p*-type Schottky-barrier heights of the Si-terminated and C-terminated SiC(001)/Ti interfaces. Results of the SiC(001)/Al interface (Ref. 12) are also listed.

SiC(001)/Ti interface	
Si-terminated	0.50 eV
C-terminated	0.22 eV
SiC(001)/Al interface	
Si-terminated	0.85 eV
C-terminated	0.08 eV

covalent interactions between the C and Ti atoms. The occupied C2p-Ti3d bonding band is separated by a shallow minimum from the unoccupied C2p-Ti3d antibonding or Ti3d nonbonding bands. The Fermi level is located at the shallow minimum, which indicates the stability of the interfacial bonds. This feature is quite different from the interface LDOS of the Si-terminated interface without any minima at the Fermi level. This feature is similar to the bulk TiC DOS, where a deep minimum separates the occupied and unoccupied C2p-Ti3d bands.[34–36] In the LDOS's below the back Si-C bond, the bulk SiC features are recovered substantially, although there exist MIGS's in the band gap.

C. Bond adhesion

Table I lists the adhesive energy of each interface, which is the energy gain per unit area in forming one interface from two relaxed (1×1) surfaces. For the Si-terminated interface, the adhesive energy is 2.52 Jm^{-2}, which is the smallest in Table I. This is consistent with a metallic character of the Si-Ti bond without strong covalent or ionic interactions. For the C-terminated interface, the adhesive energy is 8.74 Jm^{-2}, which is the largest in Table I. This is consistent with the formation of some kind of TiC compound layers at the interface as mentioned above. The absolute energy gain per (1×1) unit cell of the C-terminated interface with two C-Ti bonds is 5.11 eV, although the value for the Si-terminated one is 1.48 eV. The calculated cohesive energy of bulk TiC is 17.78 eV (Ref. 35) for one pair of Ti and C, which make six Ti-C bonds. Thus the cohesive energy for two Ti-C bonds is estimated to be 5.93 eV. It is interesting that this value is comparable to the present energy gain per (1×1) unit cell associated with the formation of two C-Ti bonds.

The present calculation of the C-terminated interface clearly shows that the surface C atoms of the C-terminated (001) surface can react with Ti atoms even at low temperature, and that some kind of TiC compound layers can be formed spontaneously only at the interface without breaking back Si-C bonds. This result is in good agreement with the experiments[7] using AES and LEED, which showed room temperature reaction of the surface C atoms of the C-terminated (001) surface with deposited Ti without breaking back Si-C bonds, as mentioned in Sec. I. Of course, the present calculations do not deal with the surface reconstruction,[8] but deal with only (1×1) surfaces and interfaces. However, the LEED experiment has clarified that the (2×2) reconstructed SiC surface is changed into the (1×1) surface by Ti deposition.[7] Thus, it is possible that the present configuration is really generated in such experiments. In any case, the strong interactions between the surface C atoms and Ti with covalent and partial ionic character shown in the present calculations should dominate the interface reactions in many applications.[2–5]

D. Schottky-barrier height

The *p*-type SBH can be obtained by supercell calculations based on the LDFT as the difference between the Fermi level and the valence-band top of the bulk SiC region, if the cell size is large enough. The *n*-type SBH is obtained by subtracting the *p*-type value from the experimental band-gap value, because the LDFT cannot reproduce the band gap correctly. Even for the *p*-type SBH value based on the LDFT, there remains a problem of a possible discontinuity in the exchange-correlation potential across the interface between different materials,[23] which should be dealt with by methods beyond the local density approximation (LDA) such as the *GW* approximation.[37] Thus, an exact quantitative determination of the SBH is not possible in the present calculation. However, it is possible to obtain the difference in the SBH for different interface configurations of the same ceramic/metal or semiconductor/metal system as shown for the $\mathrm{NiSi_2}(111)/\mathrm{Si}$ system.[23,24]

We have determined the SBH by analyzing the data of the LDOS for each interface. Results are listed in Table II. For the Si-terminated interface, the LDOS of the bulk SiC region has a small peak at the valence-band top caused by the MIGS, which makes it difficult to determine the SBH. We have decided the bulk valence-band top by the total band width from the valence-band bottom, and obtained the SBH

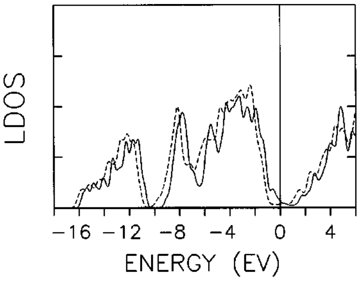

FIG. 7. Comparison between the LDOS of the central SiC region of the Si-terminated SiC(001)/Ti interface (solid line) and that of the central SiC region of the Si-terminated SiC(001)/Al interface (Ref. 12) (broken line). The difference between the valence-band top and the Fermi level indicated by a vertical line corresponds to the *p*-type SBH.

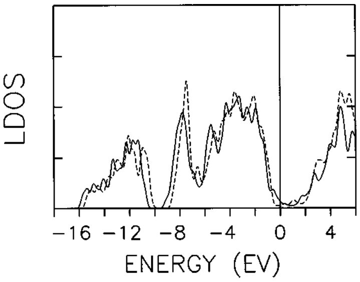

FIG. 8. Comparison between the LDOS of the central SiC region of the Si-terminated SiC(001)/Ti interface (solid line) and that of the central SiC region of the C-terminated SiC(001)/Ti interface (broken line).

of 0.50 eV. Figure 7 shows the comparison between the LDOS of the bulk SiC region of the present Si-terminated SiC/Ti interface and that of the Si-terminated SiC/Al interface.[12] It is clear that the valence band of the bulk region of the present interface is shifted upward by about 0.35 eV against the bulk band of the SiC/Al interface with the SBH of 0.85 eV. This justifies the present value of the SBH.

For the C-terminated SiC/Ti interface, the interlayer distances are expanded even at the central region in the supercell as mentioned in Sec. III B. Thus the valence-band width is reproduced to be smaller by about 0.3 eV even in the LDOS of the central SiC region, which makes it difficult to determine the SBH. However, Fig. 8 shows that the averaged shift of the valence band of the central SiC region of the present C-terminated interface is about 0.28 eV as compared with that of the Si-terminated SiC/Ti interface with the SBH of 0.50 eV. Thus, the SBH for the present interface is estimated to be 0.22 eV.

The *p*-type SBH for the C-terminated interface is smaller than that for the Si-terminated interface. The same tendency was observed for the SiC/Al interface. This difference is understood by the different interface dipole generated by different polarized charge distributions at the interfaces, similarly to the case of the SiC/Al interface. As shown in Fig. 5, the C-terminated interface has a larger charge transfer from the interface Ti atom to the interface C atom than the Si-terminated interface because of the partial ionic character of the C-Ti bond. This generates a larger dipole shift at the interface, which lowers the electrostatic potential of the Ti layers downward relatively to the SiC region, and thus lowers the *p*-type SBH. This point is similar to the C-terminated SiC/Al interface.

However, the respective values for the SiC/Ti interfaces are different from those for the SiC/Al interfaces. And the difference between the two SiC/Ti interfaces is not so large as compared with the SiC/Al interfaces. Of course, such differences between the SiC/Ti and SiC/Al interfaces should be caused by the different nature of Ti and Al. The *d* orbitals of Ti atoms induce complex features to the interfacial atomic and electronic structure as shown above. For the Si-terminated SiC/Ti interface, the charge density above the interface Si atom shown in Fig. 1 is larger than that of the Si-terminated SiC/Al interface. This may be concerned with the MIGS peak near the valence-band top attenuated rather slowly in Fig. 3. These points may cause the present *p*-type SBH lower than the Si-terminated SiC/Al interface. For the C-terminated SiC/Ti interface, the strong C-Ti bonds induce significant changes in the atomic and electronic structure as compared with the other interfaces. This should also affect the SBH.

The present dependence of the SBH on the interface structure for the same ceramic/metal or semiconductor/metal system is contrary to the traditional models for the SBH that deny such dependence.[22] In the Schottky model,[38] the SBH is determined only by the relation between the work functions of two materials, although the work function itself should depend on the surface structure. In the MIGS or charge neutrality level models,[39,40] the SBH is determined by some level in the MIGS, which is regarded to be intrinsic to respective semiconductors or ceramics. On the other hand, the dependence of the SBH on the interface structure was experimentally observed for the two types of interfaces of the $\mathrm{NiSi_2}(111)/\mathrm{Si}$ system.[41] *Ab initio* calculations[23,24] have clearly shown the mechanism of the difference, where the different interface dipole associated with the different interface charge distribution causes different SBH. Our results of the SiC/Al and SiC/Ti interfaces are essentially consistent with these results.

It should be noted that there are no firm or quantitative theories or models that can explain all the experimental results of the SBH. At least about the SBH of coherent interfaces without any misfit dislocations or defects, we think that the following two factors should dominate the SBH, in a similar way to the semiconductor heterojunction band offsets.[42] The first factor is the absolute relation between the band structure of two materials. It is possible to define reference levels or averaged potentials for respective materials, which first determine the relative position of the bands of two materials without any effects of interfaces or surfaces. This does not depend on the interface structure. The second factor is the interface dipole, which should greatly affect the connection of the two bands at the interface. This is determined by the interfacial charge distribution, and should seriously depend on the interface structure. Of course, the interface charge distribution and interface dipole are determined by the details of the interfacial atomic and electronic structure. These are very complicated in the cases of ceramic/metal or semiconductor/metal systems, unlike the rather simple atomic and electronic structure of the semiconductor heterojunction.

In comparison with the experiments, Porter and coworkers[5] have obtained the experimental SBH of the Si-terminated 6H-SiC(0001)/Ti interface. The *n*-type SBH is about 0.79–0.88 eV for as-deposited, and is about 0.86–1.04 eV for annealed. The as-deposited interface is a nearly coherent interface without reaction layers and with misfit dislocations not at the interface but at a finite distance from the interface. The *p*-type SBH of this as-deposited interface is about 2.1–2.2 eV because of the band gap of 3.0 eV. Our theoretical value for the Si-terminated SiC(001)/Ti interface, 0.50 eV, is quite different, even if we add 0.66 eV as the correction to the LDA as discussed in Refs. 9 and 43. Of course, the atomic configuration of the SiC(001)/Ti interface is quite different from that of the 6H-SiC(0001)/Ti interface. It is of much importance to perform *ab initio* calculations of the SiC(111)/Ti or 6H-SiC(0001)/Ti interfaces, which will be present in the near future. Of course, the present values of the SBH of the SiC/(001)/Ti interface may contain some errors caused by the small cell size.

Finally, it should be noted that the present interface is a coherent (1×1) interface where metallic layers are expanded along the interface. Thus, it is also important to examine the effects of misfit dislocations in future. Of course, there exist experiments indicating the presence of such coherent SiC/Ti interfaces in some conditions, and it is of much interest to examine the SBH of coherent systems as the intrinsic SBH without any extrinsic effects. Recent experiments[44] have shown that the SBH of samples with greatly reduced interfacial defects has quite different features from the SBH of usual samples.

IV. SUMMARY

The β-SiC(001)/Ti interface has been studied using the *ab initio* pseudopotential method, and compared with preceding results of the SiC(001)/Al interface. The C-terminated and Si-terminated interfaces have quite different features, similarly to the SiC(001)/Al interface. The Si-Ti bond at the Si-terminated interface has a rather metallic character similar to the Si-Al bond at the Si-terminated SiC/Al interface. The C-Ti bond at the C-terminated interface has strong p-$d\sigma$ covalent interactions between C $2p$ and Ti $3d$ orbitals like bulk TiC. The C-Ti bond length is very small like bulk TiC, although the back Ti-Ti is greatly weakened. The adhesive energy of this interface is quite large. It can be said that solid-state reaction can occur at the C-terminated interface even at low temperature. This is in good agreement with the experiments using AES and LEED, which revealed room temperature reaction of surface C atoms of the C-terminated SiC(001) surface with Ti without breaking Si-C bonds. For the Schottky-barrier height, the difference between the C-terminated and Si-terminated interfaces has a similar tendency to the SiC/Al interface, which can be explained by the difference in the interface dipole.

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