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Ab initio study of 3*C*-SiC/M (M = Ti or Al) nano-hetero interfaces

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Abstract

Ab initio pseudopotential calculation of 3*C*-SiC(1 1 1)/Al nano-hetero interfaces have been performed and interface atom species dependence (IASD) and interface orientation dependence (IOD) of nano-hetero interfaces between 3*C*-SiC ((1 1 1) or (0 0 1) orientation) and metal (Ti or Al) have been studied systematically. Stable atomic configurations of the 3*C*-SiC(1 1 1)/Al interfaces are quite different from those of the 3*C*-SiC(1 1 1)/Ti interfaces. Two terminated, Si-terminated (Si-TERM) and C-terminated (C-TERM), 3*C*-SiC(1 1 1)/Al interfaces have covalent bonding nature. In 3*C*-SiC/M (M = Ti or Al) nano-hetero interfaces, the C-terminated interface has relative strong, covalent and ionic C–Ti or C–Al bonds as TiC or SiC while the Si-terminated interface has various type of bonding nature, relative weak Si–Ti or Si–Al bonds from metallic character at the (0 0 1) interface to covalent character at the (1 1 1) interface. Adhesive energy (AE) shows strong IASD and IOD. The AE of the C-terminated interface is larger than that of the Si-terminated one. In the C-terminated interface, the AE of the (1 1 1) interface is smaller than that of the (0 0 1) one while in the Si-terminated interface there exists opposite interrelation. Schottky barrier height (SBH) also shows strong IASD and IOD. The SBH of the C-terminated interface is smaller than that of the Si-terminated one. The C-terminated SiC/Al interfaces have extremely small SBHs. In comparison with some experimental SBH, the present result is reliable as the difference of SBH between the two terminated interfaces and qualitative properties.
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Keywords: Nano-hetero interface; *Ab initio* calculation; SiC; Schottky barrier height; Pseudopotential

1. Introduction

Nano-hetero and nano-homo interfaces are one of the key issues to nano-technology in the 21st century. The most important purpose of nano-technology is just a material development with new advanced functions and high reliability in nano-order level. A well-defined SiC/metal nano-hetero interface plays an important role for nano-order development of high-performance materials as high-power, high-speed and high-temperature electronic devices and structural ceramics. It is the first essential step to clarify the atomic and electronic structures of the direct interfaces without any extrinsic effects.

An *ab initio* calculation is one of the most reasonable methods for investigating such interfaces. From the calculations, one can obtain the several important physical properties. AE, an energy benefit to the interface formation, indicates the degree of the interface toughness. SBH, an energy barrier height formed near interface between two materials, is very important factor for electronic device, because SBH often

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determines a dominant property of the device as a current–voltage interrelation.

Recently, *ab initio* pseudopotential calculations of 3*C*-SiC(1 1 1)/Ti ($(1\ 1\ 1)_{Ti}$) [1], 3*C*-SiC(0 0 1)/Ti ($(0\ 0\ 1)_{Ti}$) [2] and 3*C*-SiC(0 0 1)/Al ($(0\ 0\ 1)_{Al}$) [3] nano-hetero interfaces have been performed. The authors were treated both the C-terminated (C-TERM) interface and the Si-terminated (Si-TERM) interface to discuss the IASD and IOD. Each system shows a characteristic feature. A charge density distribution and local density of states (LDOS) of the interface indicate that the C-TERM interface has covalent and ionic bonds, and the Si-TERM interface has metallic bonds, only $(1\ 1\ 1)_{Ti}$ interface with partially covalent character. The AE of the C-TERM interface is larger than that of the Si-TERM one, thus, the former interface is stronger than the latter one. On the other hand, a p-type SBH of the C-TERM interface is smaller than that of the Si-TERM one and a difference between the two terminated interfaces is different from each system. The result can be explained by the degree of charge transfer from metal layer to SiC layer at the interface and the difference of charge distribution.

This type of interface can be directly discussed between theoretical *ab initio* calculations and experiment. Recently, a lot of SBH estimations have been done for interfaces between metal (M = Al, Ti, Ni, or Pt, etc.) and 6*H*-SiC(0 0 0 1) [4,5] and 4*H*-SiC(0 0 0 1) [6], where the atomic structure near the 4*H*-SiC(0 0 0 1) or 6*H*-SiC(0 0 0 1) surface is the same as the 3*C*-SiC(1 1 1) one. The SBHs depend strongly on IASD and IOD and the same tendency is shown as the *ab initio* calculation of the $(1\ 1\ 1)_{Ti}$ [1]. On the other hand, there exist few reports for the experiment of (0 0 1) interface by reason of the sample quality.

In this paper, we perform the *ab initio* pseudopotential calculations of 3*C*-SiC(1 1 1)/Al ($(1\ 1\ 1)_{Al}$) nano-hetero interfaces. As to the 3*C*-SiC/M (M = Ti or Al) nano-hetero interfaces, we discuss IASD and IOD, systematically. In particular, we examine that in 3*C*-SiC/M systems whether the substantial interrelation of AE and SBH between C-TERM and Si-TERM interfaces, between (1 1 1) and (0 0 1) interfaces and between Ti and Al interfaces could be existed or not. Also we make a comparison the calculated SBH with the experimental SBH and examine the SBH interrelation qualitatively and quantitatively.

2. Theoretical method

Stable atomic configurations and electronic structures are given in a framework of the *ab initio* pseudopotential method based on the density functional theory within the local density approximation (DFT-LDA). We make use of a conjugate-gradient technique by Bylander–Kleiman–Lee [7] and an effective-mixing scheme by Kerker [8] for controlling the charge-sloshing instability [9]. Present pseudopotentials are soft-type developed by Troullier and Martins [11]. The local p-component for Si, C or Al is applied to the Kleinman–Bylander separable form [10].

An appropriate supercell construction is one of the most important matters to treat the nano-hetero interface. The present supercell has three-fold symmetry (D_{3h}) and its symmetry is conserved through the atomic relaxation. Each contains a slab of 16 3*C*-SiC(1 1 1) atomic layers including a stacking-fault and two sets of four fcc-Al(1 1 1) layers as shown in Fig. 1 [1]. The stacking fault is necessary to suppress some serious problems for the SiC(1 1 1) slab such as an electric-field problem. Corresponding to the previous paper [1], we consider three groups of the atomic configurations parallel to the interface with D_{3h} symmetry: (i) Al on top of the surface atoms of SiC (T_1), (ii) Al above the hollow site of SiC (H_3), (iii) Al above the second-layer atoms of SiC (T_4). In the T_1 configuration, each interfacial Al atom interacts directly with a dangling bond of each surface atom of SiC. In the other groups, each interfacial Al atom is located on top of the center of the triangle of surface atoms of SiC and interacts mainly with three neighboring Si or C atoms. Each group contains the two kinds of stacking sequence for metal layer. Therefore, we tested the six candidates of atomic configuration model for each termination. The most stable atomic configuration with atomic relaxation normal to the interface is determined by analyzing the total energy of the supercell.

In this work, we used a parallel-type supercomputer (HITACHI SR8000 at Tsukuba Advanced Computer Center (TACC) in AIST) by developing a parallel-type program code using the data transportation library of Message-Passing Interface (MPI). After the test of energy convergence, we select 50 Ry of a plane-wave cutoff energy and 16 *k*-points in the irreducible 1/24 Brillouine zone through the self-consistent calculations and the atomic relaxations.

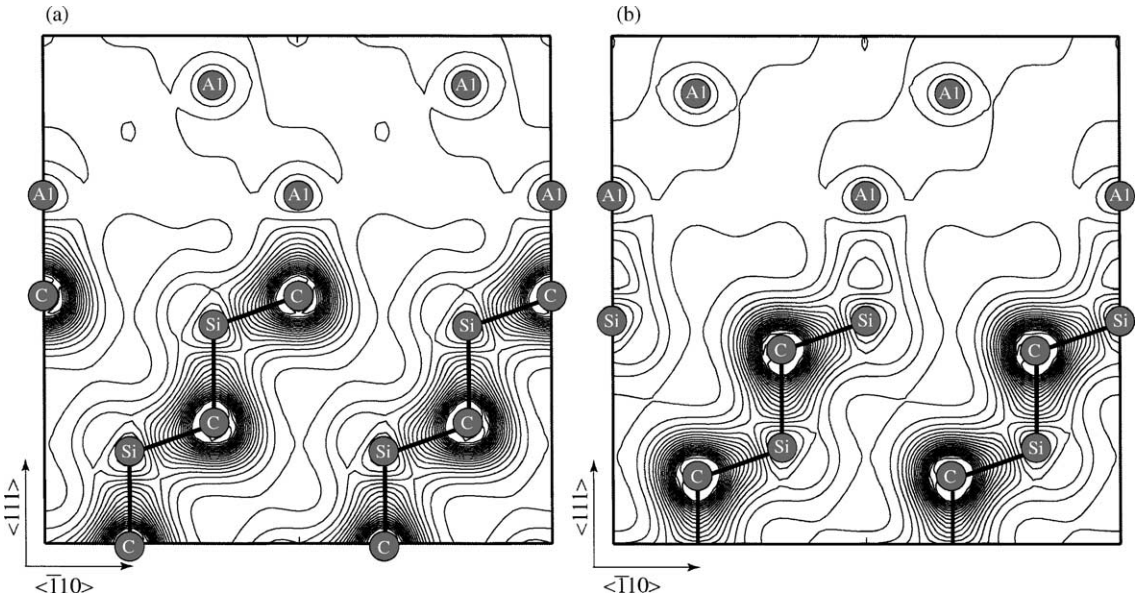

Fig. 1. Stable atomic configuration and valence charge distribution on the [−1 1 0] cross-sections for the (a) C-terminated and (b) Si-terminated 3*C*-SiC(1 1 1)/Al interfaces. All atoms are located on the same (−1 1 0) plane. Contours of the charge density is plotted from 0.001 to 0.30 a.u.$^{-3}$ in spacing of 0.015 a.u.$^{-3}$.

3. Results and discussions

3.1. Atomic configuration and charge distribution

Fig. 1 shows the most stable atomic configuration and valence charge distributions on the [−1 1 0] cross-sections for (a) C-TERM and (b) Si-TERM nano-hetero interfaces of $(1\ 1\ 1)_{Al}$. In the two terminated interfaces, the most stable site of the interfacial Al atoms is T_1 site. This is quite different from a case of $(1\ 1\ 1)_{Ti}$ nano-hetero interface that T_1 is unstable site rather than H_3 and T_4. It can be explained by bonding mechanism between SiC and metal.

In the $(1\ 1\ 1)_{Al}$ interface, each C–Al and Si–Al bond has covalent character. Each Al atom has a nearest neighbor surface atom of SiC and interacts the dangling bond directly. This atomic configuration is similar to the stacking sequence of SiC bulk. Fig. 1 indicates that the C–Al bond is similar to C–Si back bond and the Si–Al bond has a pool of the charge density as seen in a covalent bond. The bond length of C–Al is smaller than that of Si–Al bond. One would expect that the interfacial Al atoms have a character of SiC and the C-TERM interface has a strong covalent and ionic feature rather than the Si-TERM one.

In the $(1\ 1\ 1)_{Ti}$ interface [1], on the other hand, the C–Ti bond has strong covalent and ionic character as TiC and the Si–Ti bond has weak metallic with partially covalent character as Ti silicide. In this case, each interfacial Ti atom has three nearest neighbor surface atoms of SiC and adheres strongly on the SiC surface. In contrast to the $(1\ 1\ 1)_{Al}$, one would expect that the interfacial Ti atoms have a character of Ti compound.

Concerning the coordination of 3*C*-SiC(1 1 1) plane, the interfacial atoms have already three back bonds. This condition would be easy to construct the covalent bond. In the C-TERM interface, always there exists the covalent and ionic bond because of the strong interaction of C atom. On the other hand, in the Si-TERM interface IASD and IOD appear more sensitively.

Fig. 2 shows an averaged charge density on each (1 1 1) plane plotted along the (1 1 1) axis. In the two terminated interfaces, the shape of averaged charge density near the interfacial Al atom is similar to the $(0\ 0\ 1)_{Al}$ interface [3], which has a decreasing region in comparison with the other Al atoms and a small hump between the interfacial atoms. This means the

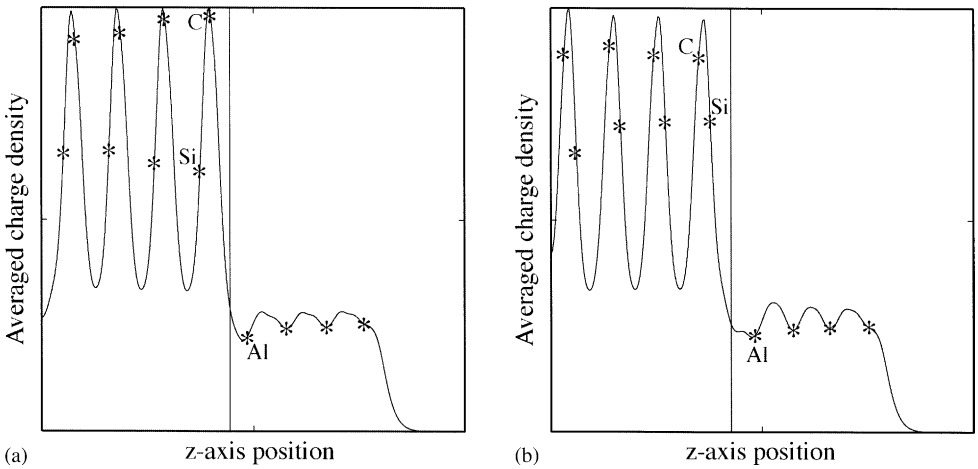

Fig. 2. Averaged charge density profile along the (1 1 1) axis of the (a) C-terminated and (b) Si-terminated 3*C*-SiC(1 1 1)/Al interfaces. The half of the supercell containing four sets of SiC layers and four Al layers with the vacuum region is shown. Asterisks indicate the positions of atomic layers. A vertical line indicates the interface.

charge transfer from Al to SiC side. The covalent character of the Si-TERM interface is not so clear in Fig. 2, however it will be shown in the LDOS analysis.

3.2. Local density of states (LDOS)

Fig. 3 shows LDOS of the $(1\ 1\ 1)_{Al}$ interface. The LDOS is calculated for each region between successive (1 1 1) layers of the supercell. In the C-TERM interface, $LDOS_{C-Al(int)}$ has a small and broad peak slightly above the Fermi level (E_F), which might be the metal-induced gap states (MIGS) [12,13]. This feature is substantially different from the $(1\ 1\ 1)_{Ti}$ interface [1] that there exists a deep valley and a large and sharp peak and from the $(0\ 0\ 1)_{Al}$ interface [3] that there exists large MIGS. As seen in Fig. 3, the small peak and the other states in the band gap only exist up to the second Si–C layers near the interface and disappear rather quickly at the third layer.

In the Si-TERM interface, $LDOS_{Si-Al(int)}$ has a valley at the E_F, differently from the $(1\ 1\ 1)_{Ti}$ [1] and $(0\ 0\ 1)_{Al}$ interface [3] that there exist large states from the superposition of the DOS of SiC and metal. Thus, one would expect that the metallic character of the interface is weak. In the 3*C*-SiC/M systems, it is interesting that only $(1\ 1\ 1)_{Al}$ interface shows non-metallic feature. In the $(1\ 1\ 1)_{Ti}$ interface, however, one can see the partial covalent feature from the LDOS analysis [1]. In the Si-TERM interface, therefore, the (1 1 1) interfaces have a covalent character more or less while the (0 0 1) interfaces have most of the metallic character.

3.3. Adhesive energy (AE)

AE is defined as the energy benefit by the formation of an interface and obtained from the difference in total energies (E_{total}) that subtract E_{total} of the relaxed (1×1) C-TERM or Si-TERM SiC surface and E_{total} of the metal surface from E_{total} of the relaxed interface. AEs are listed in Table 1 with those of the $(1\ 1\ 1)_{Ti}$, $(0\ 0\ 1)_{Al}$ and $(0\ 0\ 1)_{Ti}$ interfaces. The AE values of the C-TERM and Si-TERM interfaces are 5.47 and 4.25 J m^{-2} per one interface (2.80 and 2.18 eV/(1×1) cell), respectively. In comparison with $(1\ 1\ 1)_{Ti}$ interfaces, the energy value of the $(1\ 1\ 1)_{Al}$ interface is small in the two terminated interfaces. One can explain as follows: the interfacial Al atom mainly interacts only a dangling bond of SiC, while the interfacial Ti atom mainly interacts three equivalent surface atoms of SiC where each surface atom of SiC also interacts three Ti atoms. However, the energy difference between the two terminated interfaces is similar to.

In comparison with $(0\ 0\ 1)_{Al}$ interfaces, in the C-TERM interface (or in the Si-TERM interface) the AE of the $(1\ 1\ 1)_{Al}$ interface is smaller (or larger) than that of the $(0\ 0\ 1)_{Al}$ one if we use the unit of J m^{-2} as seen in Table 1. This interrelation is the same as the

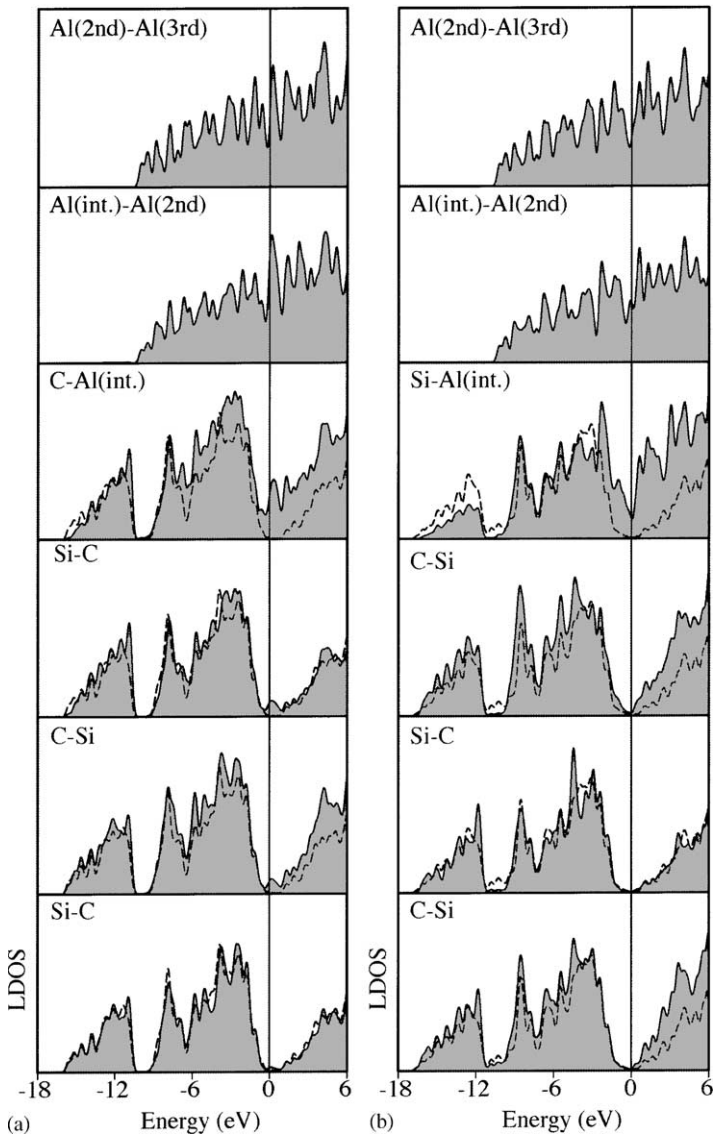

Fig. 3. Local density of states (LDOS) for the (a) C-terminated and (b) Si-terminated 3*C*-SiC(1 1 1)/Al interfaces. LDOS is given for each region between successive (1 1 1) atomic layers. Broken lines indicate the LDOS of the bulk SiC region in the supercell. A vertical line indicates the Fermi level (E_F).

case of Ti interfaces. However, the energies of the two terminated $(1\ 1\ 1)_{Al}$ interfaces are smaller than that of respective $(0\ 0\ 1)_{Al}$ interfaces if we use the unit of eV/(1 × 1) cell. It is owing to that the number of the nearest neighbor surface atom is different, where for 1 versus 1 in C-TERM and 1 versus 2 in Si-TERM, and the number of the dangling bonds, 1 versus 2 for $(1\ 1\ 1)_{Al}$ versus $(0\ 0\ 1)_{Al}$.

Consequently, the C-TERM interface is stronger than the Si-TERM one in this system and there exists the strong IASD and IOD.

3.4. Schottky barrier height (SBH)

A p-type SBH can be obtained by supercell calculations as the difference between the E_F of the metal

Table 1
Calculated bond length, adhesive energy (AE) and calculated (SBH_{cal}) and experimental (SBH_{exp}) p-type SBH for the two terminated SiC/M interfaces

	Bond length (a.u.)	AE		SBH_{cal} (eV)	SBH_{exp} (eV)
		J m^{-2}	eV/(1 × 1) cell		
$(1\ 1\ 1)_{Al}$					
C-TERM	3.8	5.47	3.21	0.06	2.22 [4], 1.3[a]
Si-TERM	4.7	4.25	2.18	0.98	2.47 [4], 1.74[b], 1.3[a]
$(1\ 1\ 1)_{Ti}$ [1]					
C-TERM	4.3	7.56	3.88	0.67	1.79 [4], 1.90 [5], 1.93 [6]
Si-TERM	4.9	6.25	3.21	1.02	2.16 [4], 2.55 [5], 2.10 [6]
$(0\ 0\ 1)_{Al}$ [3]					2.14[c]
C-TERM	3.5	6.42	3.77	0.08	
Si-TERM	4.7	3.74	2.19	0.85	0.9[d]
$(0\ 0\ 1)_{Ti}$ [2]					1.77[c]
C-TERM	3.8	8.74	5.11	0.22	
Si-TERM	4.8	2.52	1.48	0.50	

Definition of AE and SBH is denoted in the text. SBH_{exp} without [4] is estimated from the *n*-type SBH and the experimental band gap of bulk 4*H*-SiC or 6*H*-SiC.
[a] [18].
[b] [17].
[c] [19]. Polarity is unknown.
[d] [20].

region and the valence-band top (VBT) of the bulk SiC region, noted that NOT bulk SiC, analyzed from the LDOS for each interface. The reason why we use VBT in the bulk region is that the existence of MIGS near the VBT in the interface region makes it difficult to determine the SBH. No band bending occurs in the present supercell calculations because of no dopants and zero temperature condition. In this situation, the E_F only means the highest occupied level of the metal region and E_F is located somewhere into the band gap of the bulk SiC region.

Simple and traditional SBH models as Schottky [14] and MIGS and charge neutrality level [15] are often used for discussion of the interface SBH. However, it is difficult to explain the IASD and IOD of the SBH by using the models because of estimation from the bulk properties or the intrinsic level of the respective semiconductor. In previous work [1], we have already pointed out for the 3*C*-SiC/Ti interfaces that one cannot reproduce the interface SBH even if the surface effects are introduced.

Calculated p-type SBHs are listed in Table 1 with those of the $(1\ 1\ 1)_{Ti}$ [1], $(0\ 0\ 1)_{Al}$ [3] and $(0\ 0\ 1)_{Ti}$ [2] interfaces and the experimental results of the 6*H*-SiC(0 0 0 1) [4,5] and 4*H*-SiC(0 0 0 1) [6] interfaces. The values of the C-TERM and Si-TERM interface are 0.06 and 0.98 eV, respectively, and the difference is 0.92 eV. The p-type SBH of the C-TERM interface is smaller than that of the Si-TERM one. The same tendency is observed for the other SiC/M interfaces both *ab initio* calculations and experiments [1–6]. The calculated p-type SBH of the C-TERM interface is substantially small, similarly to the C-TERM $(0\ 0\ 1)_{Al}$ interface (0.08 eV). This is also small rather than the C-TERM $(1\ 1\ 1)_{Ti}$ and $(0\ 0\ 1)_{Ti}$ interfaces. In the Si-TERM interface, on the other hand, the SBH value of $(1\ 1\ 1)_{Al}$ is similar to that of $(1\ 1\ 1)_{Ti}$ (1.02 eV) and that of $(0\ 0\ 1)_{Al}$ (0.85 eV) and larger than that of $(0\ 0\ 1)_{Ti}$ (0.50 eV).

Consequently, the interface SBH is determined by the following two factors as pointed out in previous papers [1,2]: (1) interrelation of intrinsic band structures between two materials and (2) interface dipole constructed by the charge transfer and charge distribution derived from the interface polarity. The former is independent of the practical interface structure while the latter is determined by IASD and IOD.

In comparison with the experimental SBH, in the two terminated interface the calculated values are substantially small. In experiment, the interface condition is one of the important factors for SBH determination. Hara et al. [5] have pointed out the importance of interface construction by controlling the density of interfacial defects with special surface treatments. It is not so easy to estimate the intrinsic SBH value without extrinsic effects in every system, which means the SBH of the ideal interface as the present one.

In theoretical calculation, on the other hand, we use the supercell that the cell size is limited by reason of the computational resources. Thus, only coherent interface without any defects and dislocations is treated in the present study. To satisfy this condition and to absorb the lattice mismatch, the Al slab is expanded parallel to the interface about 7% which value is larger than $(1\ 1\ 1)_{Ti}$ interface (4.3%). Moreover, the DFT-LDA calculation cannot reproduce the band-gap value correctly, because of the problem of possible discontinuity in the exchange-correlation potential across the interface between two different materials. In 3*C*-SiC, some correction value (−0.66 eV) is estimated [16]. Even if the correction value is added to the calculated SBHs, it may be difficult to estimate the SBH value quantitatively within the present calculation scheme. However, the difference of SBH between the two terminated interfaces and the qualitative properties should be reliable.

4. Summary

IASD and IOD of the 3*C*-SiC/M (M = Ti or Al) interfaces have been discussed with new *ab initio* pseudopotential calculations of the $(1\ 1\ 1)_{Al}$ nano-hetero interfaces. From the analysis of the stable atomic configurations, the charge distributions, AE and LDOS, the C-TERM interface has relatively strong bonds and the Si-TERM interface has relatively weak bonds. The calculated p-type SBH of the C-TERM interface is smaller than that of the Si-TERM one. This is consistent with the recent experiments. Concerning the 3*C*-SiC/M interfaces, the Si-TERM interface has various characters from metallic to covalent while the C-TERM interface has a similar character.

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