First-Principles Calculations of Schottky Barrier Heights of Monolayer Metal/6*H*-SiC{0001} Interfaces

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Schottky barrier heights (SBHs) of monolayer metal/6*H*-SiC{0001} interfaces have been calculated by the first-principles projector augment-wave (PAW) method in order to examine the dependence on metal species as well as surface termination of SiC. Generally, *p*-type SBHs of the C-terminated (000-1) interfaces are smaller than those of the Si-terminated (0001) interfaces, because of the interface dipoles caused by substantial charge transfer. The SBHs of the Si-terminated interfaces range within a relatively narrow energy region without clear correlation with metal electronegativity, although those of the C-terminated interfaces show rather specific dependence on metal electronegativity except for systems with Fe and Co. The different dependence on the metal species for the Si- and C-terminated interfaces has been analyzed from the interface electronic structure as compared with previous theoretical models and experiments. [doi:10.2320/matertrans.47.2690]

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1. Introduction

Silicon carbide (SiC) is a wide-gap semiconductor with excellent properties for high-power, high-temperature, high-speed and low-loss electronic devices.^{1–3)} SiC has a bonding nature with both covalent and ionic characters, and has a lot of polytypes as hexagonal (2*H*-, 4*H*-, 6*H*- and more) and cubic (3*C*-) units, formed by different {0001} or {111} stacking sequence, resulting in a variety of electronic properties such as band-gap values, effective masses of electrons or holes and so on.

The Schottky barrier height (SBH) is an important factor to develop electronic devices, because the performance of electric contacts plays crucial roles in devices. The SBHs of several metal/SiC interfaces have been investigated by experimentally.⁴⁻⁹⁾ Obtained *n*-type (*p*-type) SBHs of metal/6H-SiC or metal/4H-SiC interfaces reveal a tendency of proportion (inverse proportion) to metal work functions or electronegativity, and there also exists a tendency that Cterminated (000-1) interfaces have larger (smaller) *n*-type (p-type) values than the Si-terminated ones. Of course, not all the metal species have been yet examined experimentally, and the SBH values also seem to depend on the status of interface defects seriously as shown by Hara et al.⁹⁾ However, the observed dependence of SBHs on both the metal species and the surface termination (polarity or interface stoichiometry) for metal/SiC interfaces should be involved in the essential issues of the general mechanism of SBHs at metal/ semiconductor or metal/insulator interfaces.

It should be noted that conventional theoretical models of the SBH cannot simply explain the present dependence on both the metal species and the interface structure. For example, the Schottky model¹⁰⁾ evaluates the SBH by the difference between the work function of metal and the electron affinity of semiconductor. However, the slope of the experimental SBH against the metal work function is much smaller than 1 in contradiction with the strict Schottky model, and the smaller work function (electron affinity) of the Cterminated SiC surfaces directly denies the applicability to the present metal/SiC systems.¹¹⁾ The MIGS-CNL model¹²⁻¹⁴⁾ insists on the pinning by the charge neutrality level (CNL) in the metal-induced gap states (MIGS), intrinsic to each semiconductor, which strictly denies the dependence of the SBH on either metal species or interface structure. More recently, Mönch has proposed the MIGS-electronegativity model¹⁵⁾ to explain the observed dependence of the SBH on the metal species, where the characters of metal species are expressed by Miedema's electronegativity¹⁶⁾ instead of the work function and the specific features of interface electronic structure seems to be taken into account. However, this model is also a phenomenological one containing adjustable parameters.

To explain the true mechanism of the SBH from the behavior of atoms and electrons, overcoming the above conventional or phenomenological models, the first-principles calculations based on the density functional theory (DFT) should be promising tools, although there exist difficulties concerning the interface defects caused by lattice misfit and concerning the limitation of the present DFT such as reduced band-gap widths. It is well known that the first-principles studies^{17–19)} can well explain the experimental dependence on the interface structure for the SBH of the NiSi₂(111)/Si interface²⁰⁾ through the different interface dipole. Also in our previous first-principles calculations of metal/3C-SiC interfaces,^{11,21–23)} we could successfully reproduce the dependence on the interface termination, consistently with the experimental tendency. Namely the

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C-terminated interfaces with the electron transfer from metal to SiC generally have lower *p*-type SBH values, caused by the interface dipole lowering the electrostatic potential of the metal side. From the viewpoint of the first-principles results,^{11,21–23)} the SBH seems to be determined by the two factors, first the interface dipole, dominated by the interface atomic and electronic structure (including polarity or stoichiometry), and second the intrinsic relation of the band structures of the two materials, as the band discontinuity at semiconductor heterojunctions.²⁴⁾

In this paper, we examine the dependence of SBHs of metal/6*H*-SiC{0001} interfaces on the metal species such as Al, Ti, Fe, Co, Ni, Cu, Pt and Au, systematically, using *ab initio* DFT calculations, following our previous *ab initio* studies.^{11,21–23)} Of course, we examine the C- and Siterminated interfaces for each metal species. From our viewpoint, the metal species should have effects on both the interface dipole and the intrinsic relation between the band structures of the two materials. And the effects of metal species on the interface dipole should be also dependent on the SiC surface termination. The present examination should provide valuable insights into the mechanism of the SBH and may be useful to understand the empirical applicability of the MIGS-electronegativity model.

In this work, we report SBHs of monolayer metal/6*H*-SiC{0001} interfaces as a first step toward the interfaces with metal multi-layers. To examine the intrinsic effects of the metal species, we deal with the problem of the different lattice parameters through the selection of the two types of interface cells such as (2×2) and $(\sqrt{3} \times \sqrt{3})$ so as to minimize the lattice misfit for each metal species.

2. Theoretical Method

We use the first-principles PAW method^{25–27)} based on the DFT within the generalized gradient approximation (GGA).²⁸⁾ The PAW method is a superior method with both the efficiency of the pseudopotential method and the accuracy of the all-electron method. We use the program code QMAS (Quantum MAterials Simulator).²⁹⁾ This adopts the blocked Davidson method,^{30,31)} the residual minimization and direct inversion in the iterative subspace (RMM-DIIS)^{32,33)} method and the conjugate-gradient method³⁴⁾ for the fast solution technique of eigenstates, coupled with the efficient charge-mixing method.^{35,36)} A plane-wave cutoff energy of 40 Ry is selected based on the tests of total energy convergence. In self-consistent calculations, we use three sampling k-points in the irreducible Brillouine zone of the supercell explained below.

Figure 1 shows (2×2) and $(\sqrt{3} \times \sqrt{3})$ unit cells of the monolayer metal/6*H*-SiC{0001} interfaces. In order to examine the interface polarity effect, two kinds of interfaces, C-terminated (000-1) and Si-terminated (0001) interfaces are treated. The present supercell contains a SiC slab of six C-Si bilayers with a metal (111) or (0001) monolayer on one surface. On the back SiC surface, all the dangling bonds are saturated by hydrogen atoms. Each bilayer of SiC includes eight atoms, 4 silicon and 4 carbon, in the (2×2) unit cell and six atoms, 3 silicon and 3 carbon in the $(\sqrt{3} \times \sqrt{3})$ unit cell. The metal monolayer includes four metal atoms in both



Fig. 1 Monolayer metal/6*H*-SiC{0001} interfaces with (a) (2×2) and (b) $(\sqrt{3} \times \sqrt{3})$ unit cells. Black, white and grey circles are C (or Si), Si (or C) and metal atoms, respectively.

kinds of unit cells. We determine the size of the supercell normal to the interface, namely the size of a vacuum region, by examining the total energy convergence for the increase of the size.

For the metal layer, there are several deposition sites on the surface unit cell with relatively high symmetric condition. Generally, the deposition sites affect the interface atomic and electronic structures as observed in metal/Al₂O₃³⁷⁻⁴²⁾ and metal/TiO243-45) systems. Strictly speaking, it is desirable to examine all the possible deposition sites. However, in the present study, we deal with only the deposition sites as shown in Fig. 1. In the (2×2) unit cell, all the metal atoms are located on top of the outermost SiC surface atoms. In the $(\sqrt{3} \times \sqrt{3})$ unit cell, the metal atom at the corner of the cell is located on top of the outermost SiC surface atom, and the other atoms are naturally located on top of the midpoint between the two outermost atoms. These configurations have relatively high symmetry (C_{3v}) , and this is natural selection as the first step. The purpose of the present study is to clarify the effects of each metal species. Thus it is effective to deal with common configurations to analyze the intrinsic effects of each metal species. Note that the present (2×2) unit cell is the same as the (1×1) unit cell, intrinsically. The reason why we deal with the (2×2) cell is that the present interface models can be applicable to the models of multi-layer interfaces, interface defects and intermetallic compounds for our future studies.

We use the lattice data optimized by the SiC slab calculations for the size of the supercell. The metal monolayer is expanded so as to construct a coherent interface. To minimize the magnitude of the adjustment, we select either (2×2) or $(\sqrt{3} \times \sqrt{3})$ unit cell for each metal species. Table 1 lists the lattice mismatch for each metal species. Practically, we have to deal with such coherent interfaces, because of the limitation of the computer resources to deal with general incoherent interfaces. And for the present study to examine the effects of metal species, the present simple and systematic models are rather adequate as mentioned above.

First we perform the relaxation of each interface, where the symmetry of the supercell is preserved by the constraints. Then atomic and electronic structures are analyzed in detail. In the supercell calculation, the p-type SBH is obtained by

Table 1 P-type SBHs of monolayer metal/6H-SiC{0001} interfaces. The SBHs list the C-terminated (000-1) and Si-terminate (0001) interface with experimental results (in parentheses). Difference means subtraction of SBH of (000-1) from (0001). The unit of SBH is eV. The lattice misfit indicates the misfit percentage between metal and SiC with the applied cell unit.

	Al	Ti	Fe	Со
(000-1)	0.11 (2.22 ^a)	0.33 (1.79 ^a , 2.03 ^b)	1.22	1.18
(0001)	1.09 (2.47 ^a)	1.00 (2.16 ^a , 2.19 ^b)	1.38	1.30 (1.71 ^a)
Difference	$0.98 (0.25^{a})$	0.67 (0.37 ^a , 0.16 ^b)	0.16	0.12
lat. misfit	7.1 (2 × 2)	4.3 (2 × 2)	7.2 $(\sqrt{3} \times \sqrt{3})$	$6.4~(\sqrt{3}\times\sqrt{3})$
	Ni	Cu	Pt	Au
(000-1)	0.59 (1.10 ^a , 1.41 ^b)	0.13	0.46	0.29 (1.53 ^a , 1.21 ^b)
(0001)	1.18 (1.57 ^a , 1.59 ^b)	1.41 (1.26 ^c)	1.28 (1.53 ^a)	1.05 (1.45 ^a , 1.47 ^b)
Difference	0.59 (0.47 ^a , 0.18 ^b)	1.28	0.82	0.76 (0.11 ^a , 0.26 ^b)
lat. misfit	$6.8~(\sqrt{3}\times\sqrt{3})$	$4.3~(\sqrt{3}\times\sqrt{3})$	$10.1 (2 \times 2)$	$6.5 (2 \times 2)$

^aFrom Refs. 4) and 6).

^bFrom Ref. 8) for 4*H*-SiC interfaces. The data are converted to *n*-type SBH using the band gap of 4*H*-SiC (3.28 eV).

^cFrom Ref. 15).

the difference between the Fermi level and the valence band top (VBT) of the bulk SiC region in the supercell. In this paper, we evaluate the VBT of the bulk SiC region through the analysis of the local density of states (LDOS) as previous papers.^{11,21–23)} Of course, it is desirable that the bulk region is far from the interface so that the effects of the MIGS can be neglected. The reason why we usually obtain the *p*-type value is that the conduction band bottom necessary to obtain the *n*-type value cannot be correctly calculated within the DFT-GGA. Thus we obtain the *n*-type value by subtracting the *p*-type value from the experimental band gap.

3. Results and Discussions

Figure 2 shows the LDOS of the SiC bulk region in the monolayer metal/6H-SiC{0001} interfaces to determine the SBH values listed in Table 1. In Fig. 1, one can clearly see that the VBT of the C-terminated (000-1) interface is located near the Fermi level as compared with the Si-terminated (0001) interface for each metal species, which means the former *p*-type SBH is smaller than the latter one. This should be caused by the larger interface dipole associated with larger charge transfer from the metal layer to the C-terminated surface. This is because the carbon atom in SiC has larger electronegativity than the Si atom. As listed in Table 1, this tendency is consistent with the experimental results, although the absolute SBH values are different from the experimental results.

In order to examine the correlation between the SBH and the metal species, we plot the SBHs vs. metal work functions⁴⁶⁾ and the SBHs vs. Miedema's metal electronegativity¹⁶⁾ as shown in Figs. 3(a) and 3(b). In conventional models such as the Schottky model, the metal work function is regarded as an essential factor to determine the SBH. However, we do not think this model is valid as discussed in our previous papers,^{11,21–23)} and the metal work function is determined by both the band structure effect and the surface dipole, dependent on the surface conditions, and is not a universal parameter.⁴⁷⁾ As discussed in Ref. 15), thus, it is proper to use the electronegativity to represent the intrinsic nature of each metal species, especially for the present system of only monolayer coverage. There is a positive



Fig. 2 LDOS of bulk region of SiC in monolayer metal/6*H*-SiC{0001} interfaces. The solid and dashed lines indicate the C-terminated (000-1) and the Si-terminated (0001) interfaces, respectively. The zero energy point indicates the Fermi level of the supercell.



Fig. 3 SBH plots as a function of (a) metal work functions and (b) Miedema's metal electronegativities and the difference of the electronegativities of the metal and SiC. Black and white circles are the C-terminated (000-1) and the Si-terminated (0001) interface, respectively. The data of metal work functions (Ref. 46) and electronegativities (Ref. 16) are plotted by experimental results. The dashed line indicates the MIGS line by the MIGS-and-electronegativity concept (Ref. 15).

correlation between the metal work function and the electronegativity with several exceptions.⁴⁷⁾

In Figs. 3(a) and 3(b), it is clear that the values of the C- and Si-terminated interfaces form two different groups as mentioned above. It is interesting that the lowering of the SBH value for the C-terminated interface against the Si-terminated one is much smaller for Fe and Co than the other metal species, and it is the largest for Cu. As a result, the SBH values of the C-terminated Fe and Co systems are located in the different group as exceptions.

In Figs. 3(a) and (b), the SBHs of the Si-terminated interfaces are located within a rather narrow energy region and reveal no clear dependence on the metal electronegativity or work function. On the other hand, the SBHs of the C-terminated interfaces seem to have some correlation with the metal electronegativity with the exceptions of the Fe and Co systems. There exists a proportional relationship between the *p*-type value and the metal electronegativity or work function.

Here it should be noted that this proportional relationship of the *p*-type SBH to the metal electronegativity or work function is in contradiction with the experimental results. In Fig. 3(b) we also plot the straight dashed line from the phenomenological MIGS-electronegativity model¹⁵) expressed as

$$\Phi_{Bp}^{MIGS} = 1.44 - 0.24 \cdot (X_m - X_{SiC}), \tag{1}$$

where Φ_{Bp}^{MIGS} is *p*-type SBH, 1.44 and 0.24 are parameters, and X_m and X_{SiC} are electronegativity of metal and SiC, respectively. The parameters were essentially given so as to reproduce the experimental SBH values of the Si-terminated interfaces. This indicates that the experimental *p*-type SBH values show *inverse* proportion to the metal electronegativity. Thus we have to explain the reasons why the present SBH values of both the Si- and C-terminated interfaces depend on the metal species in quite different manners from the experimental results.

The Si-terminated interfaces have a tendency to form interfacial bonds with more metallic features associated with enough MIGS than the C-terminated interfaces, as observed in our previous *ab initio* results of the Si-terminated SiC/ metal interfaces.^{11,21–23} This should be caused by the nature

of Si atomic orbitals with larger spatial extent and higher energy levels than those of carbon. Figure 4 shows the LDOSs of the interface regions of the C- and Si-terminated interfaces. By integrating the LDOS from the VBT to the Fermi level in each interface, one can estimate the quantity of occupied MIGS.⁴⁸⁾ It is clear that the Si-terminated interface has more rich MIGS than the C-terminated interface in each metal system. Thus the present less dependence of the SBH of the Si-terminated interface on the metal species should be caused by this kind of metallic features of the interfacial bond, which tends to reduce charge transfer or polarized distribution, resulting in the screening of large interface dipoles as referred as the screening by MIGS.⁴⁸⁾ In other words, the Si-terminated interfaces seem to have features similar to metal/Si interfaces, where the SBH is known to have a smaller slope parameter in Eq. (1) in a similar manner.¹⁵⁾

About the C-terminated interfaces, the positive correlation of the *p*-type SBH with the metal electronegativity can be explained by the magnitude of the interface dipole caused by the interface charge transfer, as observed in our previous *ab initio* results of the C-terminated SiC/metal interfaces.^{11,21-23)} It is clear that the charge transfer occurs from the metal layer to the C-terminated surface in each metal system, because of the lowering against the SBH of the Siterminated interface. For metal species with large electronegativity, the charge transfer from the metal layer to the Cterminated surface should be suppressed, because the electronegativity means the potential to attract the valence electrons. This should result in the smaller interface dipole and the larger *p*-type SBH value for metals with the larger electronegativity. Thus the present results are reasonable.

About the exceptions of the Fe and Co cases, the *p*-type SBH values of the C-terminated interfaces remain higher, because of the smaller lowering from those of the Siterminated interfaces as mentioned above. This feature can be explained by the nature of *d* orbitals in the middle of the transition metal series. Fe and Co tend to have strong covalent interactions with the C-terminated surface associated with strong orbital hybridization, which seems to prevent simple charge transfer, because a larger part of *d* electrons are associated with the bonding.



Fig. 4 LDOS near the interface in monolayer metal/6*H*-SiC{0001} interfaces. The solid and dashed lines indicate the C-terminated (000-1) and the Si-terminated (0001) interfaces, and dot lines indicate the LDOS in the metal region of the C-terminated interface. The zero energy point indicates the Fermi level of the supercell.

In this way, we can explain reasonably the present dependence of the SBH on the metal species for both the Si-terminated and C-terminated interfaces. In the Si-terminated interfaces, the metallic interfacial bond tends to screen the dependence on the metal species. In the C-terminated interfaces, the suppression of the charge transfer toward the SiC surface for metals with larger electronegativity causes the positive correlation with the metal electronegativity (or work function). However, as mentioned above, the present dependence is in contradiction with the experimental results. We think that this should be caused by the present models with only monolayer coverage. This point can be explained as follows. As explained in Sec. 1, we think that the SBH should be determined by the two factors; first the interface dipole and second the intrinsic relation between the band structures of the two materials. The examination of the dependence on the metal species using the present models of monolayer coverage means the examination of the effects of the metal species only on the first factor, because the metal monolayer cannot reveal usual band structure, although this can reproduce essential features of the interfacial interactions. Thus, the future examination of the dependence of the second factor on the metal species may settle the discrepancy between the *ab initio* SBH and the experiments. This problem will be dealt with by the interface models with metal multilayers in the near future.

4. Conclusion

First-principles calculations of SBHs of the monolayer metal/6H-SiC{0001} interfaces are performed, and the effects of both the interface polarity and metal species were analyzed. The *p*-type SBHs of the C-terminated (000-1) interfaces are smaller than those of the Si-terminated (0001) interfaces, because of the charge transfer. The dependence of the SBH on the metal species is different for the Si- and Cterminated interfaces. For the Si-terminated interfaces, the metallic interfacial bond tends to screen the dependence on the metal species, and for the C-terminated interfaces, the suppression of the charge transfer for metals with larger electronegativity causes the positive correlation with the metal electronegativity or work function. The present results indicate the importance of the intrinsic relation between the band structures of the two materials so as to reproduce the experimental dependence on the metal species.

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