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First-principles study of nano-hetero interfaces -semiconductor/metal and oxide/metal interfaces-

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First-principles calculations of nano-hetero interfaces for semicondoctor/metal (SiC/Ti and SiC/Al) interfaces and oxide/metal (Al_2O_3/Cu and TiO_2/Au) interfaces have been performed by the first-principles molecular dynamics method and the first-principles pseudopotential method. In SiC interfaces, the C-terminated interface is stronger than the Si-terminated one. The *p*-type Schottky barrier height (SBH) of the former interface is smaller than that of the latter one. This tendency is consistent with the recent experiments. In Al_2O_3/Cu interface, Cu-O interaction of the O-terminated interface is very strong, while Cu-Al interaction of the stoichiometric (Al-terminated) interface is rather weak. The adhesive energy of the O-terminated interface is larger than that of the stoichiometric one. A rigid-type first-principles tensile test has indicated the difference of physical properties between interlayers. TiO_2/Au interface is very important for nano catalysis. Non-defect interface do not have large charge transfer between TiO_2 and Au. On the other hand, the charge transfer from Ti to Au and from Au to O exists in O-vacancy interface and in TiO vacancy interface, respectively. One would expect that the difference of tendency of the charge transfer has close relationship with the mechanism of catalytic reaction.

Key words: nano-hetero interface, first-principles calculation, SiC, Al_2O_3, TiO_2

1. INTRODUCTION

Nano-hetero and nano-homo interfaces are very important to nanotechnology in the 21st century. The most important factor of nanotechnology is material development with new advanced functions and high reliability in nano-order level. It is the first essential step to clarify the atomic and electronic structures of the direct interfaces without any extrinsic effects.

First-principles calculation is one of the most reasonable methods for investigation of such interfaces. From the calculations, we can obtain the several important physical properties: adhesive energy (AE), Schottky barrier height (SBH) and so on. First-principles pseudopotential calculations of 3*C*-SiC(111)/Ti ($(111)_{Ti}$) [1], 3*C*-SiC(001)/Ti ($(001)_{Ti}$) [2] and 3*C*-SiC(001)/Al ($(001)_{Al}$) [3] nano-hetero interfaces have been performed; SBH estimations have been done for interfaces between metal (= Al, Ti, Ni, or Pt etc.) and 6*H*-SiC(0001) [4,5] or 4*H*-SiC(0001) [6]. The SBHs indicate the interface atom species dependence (IASD) and the interfacial orientation dependence (IOD In this paper, we perform the additional pseudopotential calculation of 3*C*-SiC(111)/Al ($(111)_{Al}$) nano-hetero interfaces and discuss IASD and IOD, systematically.

Al_2O_3/Cu nano-hetero interface is important for applications in the structure materials as thermal barrier coating and the semiconductor industry. In particular, it is very interesting to clarify the effect of interface stoichiometry. The atomic structure of the interface has been investigated by high-resolution tunnel electron microscopy (HRTEM) and their chemical and electronic nature [7,8], and by first-principles calculations [9-11]. The results indicate that the O-terminated interface ($(Al_2O_3/Cu)_O$) is energetically stable rather than the stoichiometric one ($(Al_2O_3/Cu)_{Al}$). In this paper, we also perform the first-principles calculations both two terminated interfaces and their energy analysis. Also we have carried out the rigid-type first-principles tensile test in the interface region of $(Al_2O_3/Cu)_O$.

TiO_2/Au nano-hetero interface is very important to investigate the nano-size catalyst. Haruta and co-workers [12] found that gold has catalytic activity when gold is deposited as nano-size particles on several kinds of metal oxides such as TiO_2. Why chemically stable gold is involved in the catalytic activity is very interesting issue. Akita and co-workers [13] have carried out the analytical HRTEM observation for Au on TiO_2 to obtain a structural insight into the unique catalytic property. In this paper, we investigate the adsorption of one Au ad-atom per surface unit cell on the stoichiometric TiO_2(110) surface and on the defective non-stoichiometric surfaces. Also we deal with the Ti-rich surface formed by the removal of bridging-oxygen atom (VO^B surface), and the O-rich surface formed by the removal of 6-fold titanium and bridging-oxygen atoms (VTi^6O^B surface), as well as the perfect stoichiometric surface.

2. THEORETICAL METHOD

Stable atomic configurations and electronic structures are given in a framework of the first-principles pseudopotential method based on the density functional theory within the local density approximation (DFT-LDA) or within the generalized gradient approximation (DFT-GGA). Present calculations are used for our original program package KAMIKAZE or a program package STATE (Simulation Tool for Atom TEchnology). They adopt the residual minimization scheme-direct inversion in the iterative subspace (RMM-DIIS) technique [14-16] and the conjugate gradient technique [17]. Present pseudopotentials are soft type [18] and/or ultrasoft type [19].

Appropriate supercell construction is one of the most important factors to treat the nano-hetero interface. Each supercell has reasonable symmetry and its symmetry is conserved through the atomic relaxation.

In this work, we used a parallel-type supercomputer (HITACHI SR8000 at Tsukuba Advanced Computer Center (TACC) in AIST) by a parallel-type program code using the data transportation library of Message-Passing Interface (MPI).

3. RESULTS AND DISCUSSIONS

3.1 SiC/metal interfaces

Figure 1 shows the most stable atomic configuration and valence charge distributions on the [-110] cross-sections for (a) C-terminated (C-TERM) and (b) Si-terminated (Si-TERM) nano-hetero interfaces of $(111)_{Al}$. In the two terminated interfaces, the most stable site of the interfacial Al atoms is T_1 site. This result is different from a case of $(111)_{Ti}$ nano-hetero interface [1]: H_3 or T_4 site is stable. It can be explained by bonding mechanism between SiC and metal. In the $(111)_{Al}$ interface, each C-Al and Si-Al bond has covalent character. The interface Al atom has a nearest-neighbor surface atom of SiC and forms a dimmer-like bond. This stacking sequence is similar to the bulk SiC. The bond length of C-Al is smaller than that of Si-Al bond. Concerning the present result, one would expect that the interface Al atom has a character like SiC and the C-TERM interface has a strong covalent and ionic feature rather than the Si-TERM one.

In the $(111)_{Ti}$ interface [1], on the other hand, the C-Ti bond has strong covalent and ionic character as TiC; 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 $(111)_{Al}$, one would expect that the interfacial Ti atoms have a character of Ti compound.

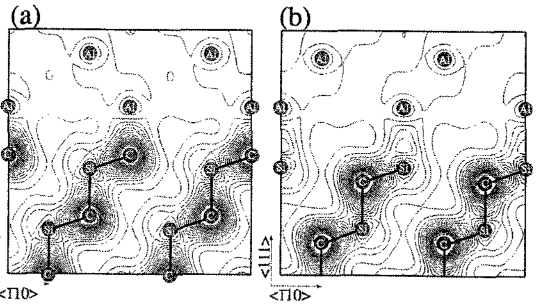

Fig. 1 Stable atomic configuration and valence charge distribution on the [-110] cross-sections for the (a) C-terminated and (b) Si-terminated 3C-SiC(111)/Al interfaces. All atoms are located on the same (-110) plane. Contours of the charge density is plotted from 0.001 a.u.$^{-3}$ to 0.30 a.u.$^{-3}$ in spacing of 0.015 a.u.$^{-3}$

Considering the coordination of 3C-SiC(111) plane, the interfacial atoms have already three back bonds. This condition would be easy to form the covalent bond. In the C-TERM interface, there exists the covalent and ionic bond because of strong reactivity of the C atom. On the other hand, in the Si-TERM interface IASD and IOD appear more sensitively.

AE is defined as energy benefit by formation of one interface and obtained from the difference in total energies (E_{total}) that subtract E_{total} of the relaxed (1x1) 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 I with those of the $(111)_{Ti}$, $(001)_{Al}$ and $(001)_{Ti}$ interfaces. The AE values of the C-TERM and Si-TERM $(111)_{Al}$ interfaces are 5.47 and 4.25 Jm^{-2} (2.80 and 2.18 eV/(1x1) cell), respectively. In comparison with $(111)_{Ti}$ interfaces, the energy value of the $(111)_{Al}$ 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.

Calculated p-type SBHs are listed in Table I with those of the $(111)_{Ti}$ [1], $(001)_{Al}$ [3] and $(001)_{Ti}$ [2] interfaces and the experimental results [4-6]. The values of the C-TERM and Si-TERM $(111)_{Al}$ interface are 0.06 eV and 0.98 eV, respectively. The p-type SBH of the C-TERM interface is smaller than that of the Si-TERM one, which is the same tendency as the other SiC/M interfaces. The calculated p-type SBH of the C-TERM $(111)_{Al}$ interface is substantially small, similarly to the C-TERM $(001)_{Al}$ interface (0.08 eV). This is also small rather than the C-TERM $(111)_{Ti}$ and $(001)_{Ti}$ interfaces. In the Si-TERM interface, on the other hand, the SBH value of $(111)_{Al}$ is similar to that of $(111)_{Ti}$ and that of $(001)_{Al}$ and larger than that of $(001)_{Ti}$.

Consequently, the interface SBH is determined by the following two factors as pointed out in previous papers [1-3]: 1) interrelation of intrinsic band structures between two materials 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, the calculated values are small. In experiment, the interface condition is one of the important factors for SBH determination [5]. However, it is not easy to estimate the intrinsic SBH value without extrinsic effects. In theoretical calculation, on the other hand, we use the limited supercell by reason of the computational resources; only coherent interface without any extrinsic factors like defects is treated in the present study. To satisfy the above condition and absorb the lattice mismatch, the Al-side slab is expanded parallel to the interface about 7% which value is larger than $(111)_{Ti}$ interface. 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 3C-SiC, some correction value (-0.66 eV) is estimated [20]. Even if the correction value is added to the calculated SBHs, it may

Table I. Calculated bond length, adhesive energy (AE) and calculated (SBH_{cal}) and experimental (SBH_{exp}) *p*-type SBH for the two terminated SiC/M interfaces. Definition of AE and SBH is denoted in the text. SBH_{exp} without Ref. [4] is estimated from the *n*-type SBH and the experimental band gap of bulk 4*H*- or 6*H*-SiC.

	bond length (a.u.)	AE (Jm^{-2})	AE (eV/(1x1) cell)	SBH_{cal} (eV)	SHB_{exp} (eV)
$(111)_{Al}$					
C-TERM	3.8	5.47	3.21	0.06	2.22[4], 1.3[b]
Si-TERM	4.7	4.25	2.18	0.98	2.47[4], 1.74[a], 1.3[b]
$(111)_{Ti}$ [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]
$(001)_{Al}$ [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]
$(001)_{Ti}$ [2]					1.77[c]
C-TERM	3.8	8.74	5.11	0.22	
Si-TERM	4.8	2.52	1.48	0.50	

[a] A. L. Syrkin et al. J. Appl. Phys. 78 (1995) 5511.

[b] K. Yasuda, T. Hayakawa, M. Saji, IEEE Trans. Electron Devices 34 (1987) 2002.

[c] J. R. Waldrop, R. W. Grant, Appl. Phys. Lett. 56 (1990) 557. Polarity is unknown.

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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.

3.2 Al_2O_3/Cu

Two terminated interfaces of the Al_2O_3/Cu nano-hetero interface are examined. In the present supercell, there are three candidate positions for the interfacial Cu atom; on top of the interface Al atom (Al-site), on top of the O Atom (O-site) and hollow site. After the atomic relaxation and energy analysis, we obtain that the most stable position of the interface Cu atom is hollow site, which is consistent with other results [9-11]. The or interlayer distance of Cu-O at $(Al_2O_3/Cu)_O$ is smaller than that of Cu-Al at $(Al_2O_3/Cu)_{Al}$. The above feature is obtained from the HRTEM observations [7,8].

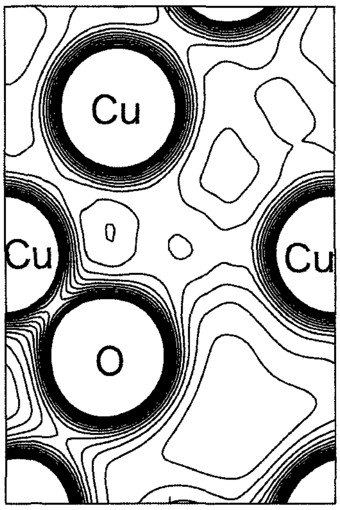

Fig. 2 Stable atomic configuration and valence charge distribution on the [11-20] cross-sections for the O-terminated $Al_2O_3(0001)$/Cu interface. All atoms are located on the same (11-20) plane. Contours of the charge density is plotted from 0.01 a.u.$^{-3}$ to 0.10 a.u.$^{-3}$ in spacing of 0.007 a.u.$^{-3}$

Figure 2 shows the stable atomic structure and the charge density distribution near the $(Al_2O_3/Cu)_O$. $(Al_2O_3/Cu)_O$ indicates the strong interaction between Cu and O atoms. One would expect to form the complicated bond with the ionic and covalent characteristics. On the other hand, $(Al_2O_3/Cu)_{Al}$ does not show the special hybridization near the interface. It can be explained that the origin of the adhesion is the electrostatic force by the imaging force model. The AE of the $(Al_2O_3/Cu)_O$ is larger than that of the $(Al_2O_3/Cu)_{Al}$. This is consistent with recent studies [7-11].

The rigid-type first-principles tensile test is carried out for the $(Al_2O_3/Cu)_O$, where "rigid-type" means "without relaxation after supercell expansion". First, the electronic structure is calculated by using the stable atomic structure. Second, the supercell is expanded normal to the interface with the atom position replacement. Third, the electronic structure is re-calculated by using the expanded supercell and replaced atomic structure. A change of the charge density distribution shows that the interfacial bond charge disappears when the interlayer distance expands about 1.1~1.3 Å from the stable interlayer distance. The total energy increased with supercell expansion and its increase stopped after about 1.8~2.0 Å interlayer expansion. This saturation is because the interface is separated into almost two surface slabs.

3.3 TiO_2/Au

The adsorption of one monolayer of Au atoms (one Au ad-atom per surface unit cell) on the relaxed $TiO_2(110)$ 1×1 surfaces was examined. Five-possible adsorption sites (A to E) were examined for the stoichiometric surface and six-possible adsorption sites (A to F) were examined for the VO^B and VTi^6O^B surfaces. The positions of the adsorbed Au and the substrate atoms were optimized according to their atomic forces.

Table II. Adsorption energy, E_{ad}, of Au on the $TiO_2(110)$ surfaces. Unit is eV/adatom.

	Type A	Type B	Type C	Type D	Type E	Type F
Stoichiometric	-0.014	0.103	0.043	0.101	0.024	
VO^B	1.501	0.522	0.548	1.900	1.507	1.904
VTi^6O^B	4.246	0.312	0.820	3.611	4.239	2.547

Table II lists the adsorption energies, which are defined as $E_{ad}=(E_{TiO2}+E_{Au}-E_{TiO2/Au})$, where E_{Au}, E_{TiO2}, and $E_{TiO2/Au}$ represent the total energies of a free Au monolayer, the clean $TiO_2(110)$ surface, and adsorbed system, respectively. Most stable adsorption site is B or D for the stoichiometric surface, D or F for the VO^B surface, and A or E for the VTi^6O^B surface. However, sites D and F for the VO^B surface are converged to the same structure; sites A and E for the VTi^6O^B surface are converged to the same one after the relaxation.

For the stoichiometric surface, E_{ad} is small. This means that the interfacial interaction between the Au monolayer and the stoichiometric $TiO_2(110)$ surface is very small. The E_{ad} for the non-stoichiometric surfaces, 1.90 eV/ad-atom for the Ti-rich VO^B surface and 4.24 eV/ad-atom for the O-rich VTi^6O^B surface, are larger than the one for the stoichiometric surface, 0.10 eV/ad-atom. It can be said that the interfacial interaction between the Au monolayer and the substrate for the defective non-stoichiometric surfaces is stronger than that for the stoichiometric surface. It can be also shown by the examination of the electron transfer between the substrate and the Au ad-atom.

To investigate the electron transfer between the $TiO_2(110)$ surface and Au ad-atom, we have calculated the integrated charge density difference (ICD). The charge density difference is obtained by subtracting the superposition of the charge density of the Au monolayer and the $TiO_2(110)$ slab from the $TiO_2(110)$/Au interface. Then the ICD is calculated for each atom by integrating the charge density difference inside the sphere placing the center on the atomic position with radius 1.38 Å, 0.741 Å, and 1.38 Å for Ti, O, and Au, respectively. For the stoichiometric surface, the electron transfer is very small. For the Ti-rich VO^B surface, the electrons transfer from Ti^6 to Au. Therefore, the Au atom becomes slightly negative. For the O-rich VTi^6O^B surface, the electrons transfer from Au to O^P and the inner oxygen atoms. Therefore, Au atom becomes positive. It seems that the Au ad-atom mainly interacts with Ti^6 atoms for the VO^B surface and that the Au ad-atom mainly interacts with O^P atoms for the VTi^6O^B surface.

3. SUMMARY

First-principles calculations of nano-hetero interfaces for semicondoctor/metal (SiC/Ti and SiC/Al) interfaces and oxide/metal (Al_2O_3/Cu and TiO_2/Au) interfaces have been performed by first-principles molecular dynamics method and first-principles pseudopotential method. Each interface has various properties within the same material as seen in the first-principles calculations and the experiments. The nano-hetero interface plays an important role in the nanomaterials. It is essential to clarify the practical interface structure and design the advanced nano-hetero interface for new material development.

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