Comparison of Stability of Metals Adsorbed on SiC Surfaces: A First-Principles Study

Junko Ishii, Shigenori Matsushima

Abstract

In this study, we investigate the structural and electronic properties of metal adsorption, when metal atoms (Ni, Pt, Pd, Cu) were adsorbed on 4H-SiC (0001) and ((000$\bar{1}$) using first-principles band calculations. When metal adsorption is Ni, structural optimization calculations were performed assuming three types of adsorption sites for both 4H-SiC (0001) and (000$\bar{1}$). On the both of SiC (0001) surface and SiC (000$\bar{1}$)surface, there are both sites where metal adsorption is stable and not stable. Among them, metal adsorption properties were stabile when the metal position was equidistant to three Si or C atoms in the outermost layer.

Subsequently, calculations were performed on four type of adsorption metals (Ni, Pt, Pd, Cu) on SiC surface. In the case of the SiC (0001) plane, the adsorption energy of Pd and Pt was reduced by about 2-3 times as compared to that of Ni and Cu. Further, we found that the (0001) plane and the metal are covalently adsorbed, and when the amount of charge transfer between the metal and the SiC surface increases, the adsorption energy decreases, causing stability of metal adsorption. On the other hand, in the case of SiC (000$\bar{1}$) surface, the surface and the metal are ionic bonded, and the influence of the type of metal on the bond structure is smaller than that of the (0001) surface.

1. Introduction

SiC is one of the typical compound semiconductors. SiC has superior characteristics such as a larger dielectric breakdown electric field and a larger bandgap in comparison with silicon (Si). Recently, automated driving technology for automobiles has undergone a revolutionary evolution. Therefore, SiC, which can be used under higher voltages and currents than Si, is attracting attention. In particular, research and development on SiC-based metal-oxide-semiconductor field-effect transistor (MOSFET) has been active [1-3]. When SiC is used as a semiconductor material for transistors, adhesion to metal wires wired on the semiconductor substrate is an important parameter. However, there remains a lack of basic understanding of the adhesion between the SiC substrate surface and the metal wire. SiC substrates with a hexagonal structure, 4H-SiC and 6H-SiC, have two types of surfaces, which are SiC (0001) and SiC (000$\bar{1}$). The SiC (0001) surface is called the Si-face because the outermost layer of the surface is composed of Si atoms and has specific structures like a ($\sqrt{3}\times\sqrt{3}$) R30°and a ((6$\sqrt{3}\times$6$\sqrt{3}$) R30° [4-6]. On the other hand, the SiC (000$\bar{1}$) surface is called the C-face because the outermost layer of the surface is composed of C atoms and has a 2 × 2 and a 3 × 3 structures [7-9]. These two SiC surfaces exhibit quite different properties, needless to say. Therefore, it is essential to verify the adhesion between the two types of SiC surfaces and the metal wire.

In this study, we use a first-principles energy band calculation to verify where on the two types of SiC surfaces metal atoms are most likely to adsorb. We selected Ni, Pt, Pd, and Cu as an adsorbed atom on the SiC surface, which are frequently used as a plating metal.

2. Calculation method

Two slab models Si-rich SiC (0001) planes (type-I) and C-rich SiC (000$\bar{1}$) planes (type-II) were constructed using 4H-SiC with a hexagonal close-packed structure (**Figure 1** (a) and (b)). These models have a ($\sqrt{3}\times\sqrt{3}$) R30° structure and a thickness of 5 bilayer films [10]. The lattice constants of the slab are a = 6.1694 Å and c = 25.7210 Å, which include 20 Si atoms, 20 C atoms, and 4 hydrogen atoms. Optimization calculations for the lattice constants and atomic positions were performed within the framework of the generalized gradient approximation (GGA) [11] using the CASTEP program [12]. The valence electrons are treated non-local ultra-soft pseudopotentials (Vanderbilt-type [13]), and the cutoff energy of the plane-wave expansions was set to 600 eV. Reciprocal space integration in the first Brillouin zone (FBZ) was performed by selecting 13 irreducible k points from a 5 × 5 × 1 k-grid using the Monkhorst-Pack scheme [14]. **Figure 2 (a)** shows the adsorption sites of metal atoms on a Type I surface. Three adsorption sites are assumed here, and each site is referred to as site-1, site-2, and site-3. Site-4, Site-5, and Site-6 were set for the Type II surface, as shown in **Figure 2 (b)**. In the metal adsorbed slab model, only the atomic positions were optimized.

3. Result and discussion

Two types of SiC slab models were constructed using 4H-SiC First, we evaluated the displacement of surface atoms in the z-axis direction of type-I and type-II before and after optimization calculation. There are four outermost Si atoms (Si1, Si2, Si3, and Si4) on the surface of type-I and four outermost C atoms on the surface of type-II. The magnitudes of the displacement (Δ) on the surface of type-I were Δ (Si1) = -0.3992, Δ (Si2) = 0.059, Δ (Si3) = 0.1052, and Δ, (Si4) = 0.1074 Å respectively. On the other hand, the displacements of the four C atoms (C1, C2, C3, C4) were respectively -0.1888, -0.1886, -0.1886, and -0.187 Å on the surface of type-II. After the relaxation calculation, total energies of type-I
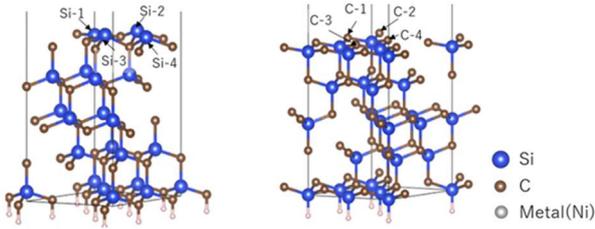
Fig. 1 4H-SiC (0001) surface model (type-I) (a) and 4H-SiC (000$\bar{1}$) surface model (type-II) (b) were optimized by relaxing atomic positions. The lattice parameters of type-I and type-II are same and are $a = b = 6.1694$, $c = 25.7210$ Å, $\alpha = \beta = 90.0°$, and $\gamma = 120.0°$.

(a) site-1　　(b) site-2　　(c) site-3
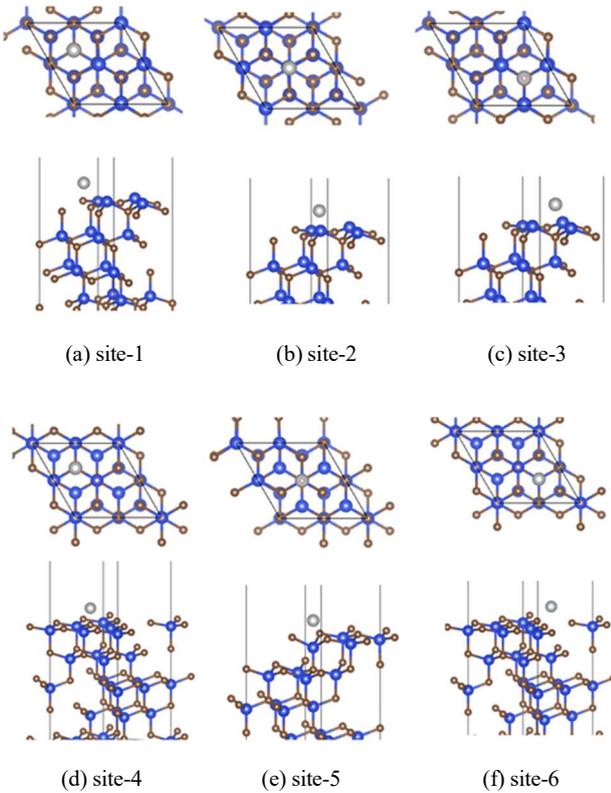
(d) site-4　　(e) site-5　　(f) site-6

Fig. 2 Ni adsorption sites on the surfaces of type-I (a) to (c) and type-II (d) to (f).

and type-II reduced by 0.5973 eV and 1.362 eV, respectively.

Then, the atomic coordinates of type-I and type-II models on which a Ni atom was adsorbed were optimized. Here, the adsorption energy (Ead) was estimated in order to compare the energetic stability between the adsorption sites. Ead is defined as follows:

$$E_{ad} = E_{total} - E_A - \mu_x \qquad (1)$$

where Etotal and EA are the total energies of the Ni-adsorbed and unadsorbed slabs, respectively, and μx is the energy per one Ni atom.

Table 1 shows the adsorption energy of a Ni atom estimated using Eq. (1) on the surfaces of type-I and type II. At site-1 and site-3, the

Table 1 Adsorption site, adsorption energy, and distance between Ni atom and SiC surface.

	Model	Metal adsorption Enargy (eV)	Distance with the adjacent atom (Å)		
Before Giometry Optimization	site-1	0.3107	-	-	-
	site-2	5.5209	-	-	-
	site-3	-0.5177	-	-	-
	site-4	3.3066	-	-	-
	site-5	2.1125	-	-	-
	site-6	0.3812	-	-	-
After Giometry Optimization	site-1	-0.6181	2.3191	2.3195	2.3198
	site-2	-0.5966	2.3082	2.3087	2.3093
	site-3	-0.5966	2.3081	2.3085	2.3086
	site-4	1.0504	1.8289	-	-
	site-5	-0.1733	2.1157	2.1175	2.1156
	site-6	-0.8451	2.0393	2.0393	2.0393

Ni atom was located approximately equidistant (2.3 to 2.4 Å) from the outmost three Si atoms. The adsorption energies in these cases were negative. The negative value means that the adsorption state is stable on the surface of type-I. In contrast, the adsorption energy on site-2 showed a positive value, suggesting that the adsorption state is unstable. In type-II, the Ni atom has the similar distances from the outermost three C atoms at site-5 and site-6. These adsorption energies were also negative, whereas at site 4, the Ni atom was adsorbed close to one surface carbon, and its adsorption energy was positive. From the comparison of adsorption energies, it is clear that the Ni atom exists most stably at site-1 and site-6 on the type-I and type-II surfaces, respectively. Subsequently, we investigated how the adsorption energy changes depending on the type of metal atom M (M = Pt, Pd, Cu). As described above, the most stable site-1 and site-6 were used as the metal adsorption site to build M-adsorbed models. Then, the M-adsorbed models were optimized by relaxing atomic positions only.

Table 2 summarizes the adsorption energy and the adsorption site. The adsorption energies were estimated based on the equation (1). Also, those adsorption energies were negative values, indicating clearly that the M forms a steady adsorption. The adsorption energy at site-1 of type-I increased in the order of Pt → Pd → Cu → Ni. The absolute values of the adsorption energy of Pd and Pt were respectively about twice and about three times that of Cu and Ni. On the other hand, the adsorption energy at site-6 increased in the order of Ni → Pd → Pt → Cu. However, the difference in the adsorption energy was smaller in comparison with the case of site-1. electron density difference using Ni-adsorbed type-I and type-II models.

Figure 3 shows the charge density difference obtained at site-1 and site-6 on the surfaces of type-I and type-II. In Fig. 3, blue areas represent charge increase. The charge accumulates primarily in the areas between Ni atom and Si atom on SiC (0001) surface. This

means that Ni atom and Si atom have a covalent bond.

On the other hand, on the SiC (000$\bar{1}$) surface, the charge around the C atom is increasing, it means that the ionic interaction is stronger from Ni adsorption.

These mean that when quantity of the charge transfer increases, adsorption energy is lower, and it have higher stability. Whereas, in the case of site-6, we could not find that significant difference between the metal charge and the adsorption energy.

Table 2 Adsorption energies of Ni, Pd, Pt, and Cu toms at site-1 and site-6 on SiC surface.

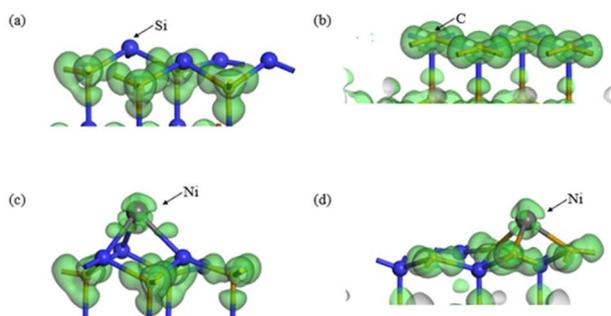| site	M	Adsorption energy (eV)
site-1	Ni	-0.6181
	Pd	-1.2877
	Pt	-2.0919
	Cu	-0.6185
site-6	Ni	-0.8451
	Pd	-0.8445
	Pt	-0.6095
	Cu	-0.4719

Fig. 3 Valence electron density differences on the surfaces of type-I (a), type-II (b),Ni atom at site-1of type-I (c), and Ni atom at site-6 of type-II (d).

4. Conclusion

We investigated the adsorption energy and electronic state when metal is adsorbed on the SiC (0001) and SiC (000$\bar{1}$) surfaces. We found that the metal adsorption energy differs depending on the adsorption position, and there are sites that are stable or not. In particular, the metal adsorption was stable when the metal position was equidistant from the three Si or C atoms on the outermost layer of the surface.

We also investigated the case of four types of metals (Ni, Pt, Pd, Cu) was adsorbed on SiC, difference of adsorption energy depends on not only the adsorption surface (SiC (0001) or SiC (000$\bar{1}$)) but also the type of metal. Metals were covalently adsorbed on the SiC

(0001) surface and ionic-bonded on the SiC (000$\bar{1}$) surface. Furthermore, in the case of SiC (0001) surface, it was shown that amount of charge transfer varies depending on type of metal, which affects the adsorption stability. Among Ni, Pt, Pd, and Cu, it was found that Pt was the most stable when it adsorbed on SiC (0001) surface.

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