Investigation of Hf Adatom Adsorption on Graphene Using Density Functional Theory Calculations*

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Density functional theory calculations of various atomic species on a graphene sheet are investigated as prototypes for the formation of nanostructures on graphene. These studies discuss the adsorption and migration energy when an adatom is adsorbed on graphene. In this study, we performed calculations regarding the adsorption of Hf atoms on graphene for several different coverages and geometries, because Hf has attracted attention as a buffer layer when a compound is grown on graphene. The calculations were performed for adatoms at three sites having BRIDGE, HOLLOW, or TOP symmetries on $3 \times 3$ and $2 \times 2$ supercells for coverages of 0.056, 0.111, 0.167, 0.25, and 0.375. The results indicated that when Hf atoms are adsorbed on the HOLLOW site, the adsorption energy tends to increase, and the subsequent metastable adsorption is a TOP-site adsorption. The most stable structure with a coverage of 0.375 is when two Hf atoms are adsorbed on the TOP site and one Hf atom is adsorbed on the HOLLOW site. Interestingly, the most stable adsorption structure for a coverage of 0.375 is hcp-Hf [0001], the same as that of the surface. [DOI: 10.1380/ejssnt.2012.325]

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I. INTRODUCTION

Graphene, a well known two-dimensional material composed of carbon atoms, is the basic material used to form nanotubes, fullerene, and graphite. Graphene has attracted much attention not only because of its role in nanocarbons but also for its own interesting electronic and mechanical properties [1–3]. In the past decade, the most significant problem regarding graphene has been the fabrication of wide and high-quality graphene sheets. Nowadays, good-quality graphene can be fabricated in laboratories, for example, using the SiC(0001) surface. Thus, one of the next steps in graphene research is the fabrication of nanostructures on a graphene plane [4]. Recently, Fujioka et al. succeeded in growing GaN on graphite using pulsed laser deposition (PLD), and they successfully fabricated a light emission diode using GaN on graphite [5–11]. Since graphite is essentially a stack of many graphene planes, similar growth is expected to be possible for graphene if the graphene plane is supported mechanically with some other material. Such growth is not limited to GaN, and there are many other possible materials that can be used to form nanostructures, nanodevices, or thin films on a graphene plane. An understanding of the mechanism of adatom adsorption by graphene is indispensable for understanding the growth of the compounds on graphene or graphite. In experiments, adatom adsorption on graphene has been reported for some, but not all, atomic species [12–18]. To apply graphene for such a purpose, we first need to thoroughly investigate the interaction between adatoms and the graphene plane. Studies have been conducted on this topic [19–22], but these studies only conducted calculations for monatomic adsorption. The aim of the present study is to discuss the stability when multiple atoms are adsorbed. In other words, we discuss the stability when the coverage of the adatom on the graphene is changed. As for the next discussion of single-atom adsorption, it should be discussed by the adsorption of multiple atoms. Some research on the coverage change in graphene has been reported [23, 24]. However, few studies have discussed the coverage change with Hf adsorption on graphene, so in this research, we chose to study the adsorption on graphene with Hf atoms as the adatoms. Hf is an important material in semiconductor devices, wherein it is used as a gate insulator. Typically, HfO$_2$ is expected to serve as the insulator film in graphene transistors. In addition, calculations for GaN growth on graphene or graphite have yielded a stable solution for N polarity [25–27]. It is expected as a buffer layer for high-quality GaN growth [28–30]. However, so far, Hf atomic adsorption on graphene has not been studied. In this study, we discuss the stability when multiple Hf atoms are adsorbed on graphene.

II. CALCULATION METHOD

In this work, we used a first-principles band calculation technique based on density functional theory (DFT). We used the Vienna Ab initio Simulation Package (VASP) [31–34], which is a high-precision first-principles calculation code based on the projector augmented wave (PAW) [35, 36] method. We adopted local spin density approximation (LSDA) as the term exchange correlation with a cutoff energy of 500 eV, and all calculation were carried out considering spin polarization. Because the coverage changes from 0.056 to 0.5, we adopted two unit cells for the graphene sheet: $3 \times 3$ and $2 \times 2$. For the lattice constant of graphene, we used the value optimized by the calculation, 2.61 Å. This is the result of lattice relaxation for a coverage of 0.5 when graphene is maximally warped. The final potential is constructed self-consistently from eigenstates at 13 sampling $k$ points in the irreducible Brillouin zone (IBZ). To obtain the final

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FIG. 1: Relaxed geometries at different Hf/C coverage ratios. (a) The structure and adsorption site after relaxation calculation with a coverage of 0.056. For the calculation of the Hf atom at certain sites, the position coordinate of the Hf atom parallel to the surface is fixed and the coordinate normal to the surface is fully relaxed. The number of figures shows a site number. (b)–(e) Structures after the relaxation calculation for coverages of 0.111, 0.167, and 0.375. The position coordinate of the Hf atom and surface is fully relaxed.

band structure, we selected 164 sampling $k$ points in the IBZ. For the calculation of adatoms at several sites, the coordinate normal to the surface is fully relaxed. One atom at the edge of the $3 \times 3$ or $2 \times 2$ structure of the graphene sheet is fixed during the relaxation of the other carbon atoms of the sheet. As a result of the relaxation calculation, the construction converges to the 12 patterns shown in Fig. 1. These sites are local stable structures for each coverage. The final calculation is carried out at a representative site for each coverage. We calculated the adsorption energy $E_{ad}$ of the atoms adsorbed on the graphene sheet from the formula

$$E_{ad} = -(E_{total} - E_{graphene} - n_{Hf}E_{Hf}),$$

where $E_{total}$ is the total energy, $E_{graphene}$ is the total energy of one graphene sheet, $E_{Hf}$ is the total energy of an isolated atom of Hf, and $n_{Hf}$ is the number of Hf atoms.

III. RESULTS AND DISCUSSION

Figure 1 shows the local stable structure for Hf atom adsorption on graphene for each coverage. The adsorption energy for each local stable structure, the magnetic moment, and the average distance between graphene and the adatom are listed in Table I. At a coverage of 0.375 more atoms make up the second layer. We do not discuss a coverage of 0.5 in this research.

Figure 1(a) shows the adsorption result for a coverage of 0.056. In other words, a coverage of 0.056 results in monoatomic adsorption in a $3 \times 3$ supercell. The adsorption energy and the migration energy of monoatomic adsorption in a $3 \times 3$ graphene cell has been discussed in detail in previous research [20, 22]. First, we calculate the density of states and the potential energy surface when a Hf atom is adsorbed on graphene for a coverage of 0.056. In addition, we discuss the details of monoatomic adsorption, and compare the stability of 0.056 coverage with that of other coverages. For a coverage of 0.056, the adatom relaxed only along the $z$ axis direction, and the adsorption sites considered were B (BRIDGE), H (hexagonal HOLLOW), and T (TOP). The most stable adsorption site for a coverage of 0.056 is the HOLLOW site, and the migration energy is about 1 eV.

The density of states (DOS) and local density of states (LDOS) at the HOLLOW site for a coverage of 0.056 are shown in Fig. 2. Figure 2(a) shows the total density of states. Figure 2(b) shows the DOS of site 8, at which a Hf atom is adsorbed on the HOLLOW site.
TABLE I: Calculation results showing the adsorption energy $E_{\text{ad}}$, $E_{\text{ad}}$ per Hf, and the magnetization (the mean value of the magnetic moment of the adatom). Height refers to the distance between graphene and the adatom.

| Coverage | Adsorption site          | $E_{\text{ad}}$ (eV) | $E_{\text{ad}}$ per Hf (eV) | Magnetization ($\mu_B$) | Height (Å) |
|----------|--------------------------|-----------------------|----------------------------|-------------------------|------------|
| 0.056    | BRIDGE                   | 2.56                  | 2.56                       | 0.000                   | 2.05       |
|          | HOLLOW                   | 3.63                  | 3.63                       | 0.200                   | 1.65       |
|          | TOP                      | 2.67                  | 2.67                       | 0.000                   | 2.12       |
| 0.111    | Dimmer HOLLOW            | 9.84                  | 4.92                       | 0.000                   | 1.82       |
|          | Homogeneous HOLLOW       | 8.64                  | 4.32                       | 0.000                   | 1.82       |
| 0.167    | Homogeneous BRIDGE       | 11.82                 | 3.92                       | 0.000                   | 2.05       |
|          | Homogeneous HOLLOW       | 14.67                 | 4.89                       | 0.000                   | 1.83       |
|          | Homogeneous HOLLOW and TOP | 14.94             | 4.98                       | 0.000                   | 1.84(T), 2.15(H) |
|          | Trimer HOLLOW            | 16.38                 | 5.46                       | 0.000                   | 1.87       |
|          | Trimer TOP void carbon centered | 15.12         | 5.04                       | 0.000                   | 2.18       |
|          | Trimer TOP carbon centered | 14.88             | 4.96                       | 0.000                   | 2.19       |
| 0.375    | HOLLOW and TOP           | 19.77                 | 6.59                       | 0.000                   | 2.22(T), 1.95(H) |

and 2(d) respectively show the $s$ and $p$ orbitals of the LDOS of site 19, at which a Hf atom is adsorbed on the HOLLOW site, and the $d$ orbitals of the LDOS of site 19, at which a Hf atom is adsorbed on the HOLLOW site. Site 8 and site 19 are shown in Fig. 1(a). In Fig. 2, the Dirac point is shifted by $-1$ eV. The adatom dopes an electron in graphene. The charge transfer from a Hf atom to a C atom is explained by the difference between their electronegativity. The charge transfer in Hf atomic adsorption can be understood from an analysis of the Bader component of the C atom and the electron in graphene. The charge transfer from a Hf atom appears at the Fermi level. This is a well-known phenomenon in the adsorption of transition metals. In the monoatomic adsorption of Hf, no band gap is open because the $d$ orbital of the Hf atom appears at the Fermi level. This is a well-known phenomenon in the adsorption of transition metals. In addition, there is no open band gap in certain chemical adsorptions, such as H atomic adsorption and S atomic adsorption, a band gap is open. However, in the monoatomic adsorption of Hf, no band gap is open because the $d$ orbital of the Hf atom appears at the Fermi level. This is a well-known phenomenon in the adsorption of transition metals. In addition, there is no open band gap in certain chemical adsorptions, such as K atomic adsorption. The $p_z$ component of the C atom and the $d_{xy}$ and $d_{xz}$ components of the Hf combine to form a hybridized orbital at $-2.5$ eV. The $s$ orbital of the Hf atom and the $p$ orbital of the C atom form a hybridized orbital around $-6$ eV. The magnetic moments are listed in Table I; the magnetic moment $\mu_B$ is $0.209$ for HOLLOW-site adsorption for a coverage of 0.056.

Magnetic moment develops the monoatomic adsorption of the Hf as well as adsorption of Ti atom and the Zr atom. The magnetic moment is constructed mainly from orbitals located on the Fermi surface. The valence electrons of Hf consist of one $d$ electron and one $s$ electron. In the HOLLOW-site adsorption of Hf, the magnetic moment of Hf is $0.078\mu_B$ for $s$, $0.054\mu_B$ for $p$, and $0.076\mu_B$ for $d$. There is almost no electron contribution to these magnetic moments around the Fermi surface. In the adsorption of Hf to graphene, the magnetic moment does not almost develop, because the valence electron is almost contributing to a bond.

The potential energy surface (PES) of Hf adsorption on graphene is shown in Fig. 3. The hexagonal shape shown in Fig. 3 corresponds to the six-membered ring of graphene. We denote the most unstable adsorption site as a zero in Fig. 3 and represent it with a warm color. The number of figures shows the energy difference in eV. These calculations show that the center of the six-membered ring (HOLLOW site) is the most stable. The PES calculations also indicate that the BRIDGE site is the most unstable when one Hf atom is adsorbed on a six-membered ring. The unstable BRIDGE site takes the local stable state, because this state is the saddle point. Therefore, the Hf atom adsorbed on this BRIDGE site moves to the other sites easily, but the BRIDGE site is locally stable. In contrast, BRIDGE-site adsorption is the most stable for the adsorption of B, C, N, and O atoms on graphene [19, 20, 22].

Figure 1(b) shows the adsorption result for a coverage of 0.111. For the calculation of adatoms at several sites, the coordinate normal to the surface is fully relaxed. One atom at the edge of the $3 \times 3$ structure of the graphene sheet is fixed during the relaxation of the other carbon atoms of the sheet. When Hf atoms are adsorbed, for a coverage of 0.111, two local stable structures exist. When Hf atoms are adsorbed on the adjoining HOLLOW site, we use the model named “Dimmer HOLLOW.” When Hf atoms are adsorbed homogeneously in the HOLLOW site, we use the model named “Homogeneous HOLLOW.” The Dimmer HOLLOW structure is the most stable for a coverage of 0.111. The adsorption energy per Hf atom is 4.92 eV, and the energy difference between the Homogeneous HOLLOW structure is about 0.7 eV. In the Dimmer HOLLOW structure, it is more slightly than homogeneous structure stabilized, because the interaction between neighboring Hf atoms is greater in the Dimmer HOLLOW structure.

Figure 1(c) shows the adsorption results for a coverage of 0.167. For the calculation of adatoms at several sites, the coordinate normal to the surface is fully relaxed. One atom at the edge of the $3 \times 3$ structure of the graphene sheet is fixed during the relaxation of the other carbon atoms of the sheet. For a coverage of 0.167, we obtain six kinds of local stable structures. These structures are classified as either the homogeneous type or the trimer type. The first type consists of homogeneous model adsorbed on the HOLLOW or BRIDGE site. We name the three local stable structures “Homogeneous BRIDGE,” “Homogeneous HOLLOW,” and “Homogeneous HOLLOW and TOP.” The second type consists of a trimer model ad-
FIG. 2: Density of states (DOS) and local density of state (LDOS) at the HOLLOW site for a coverage of 0.056. The site numbers are indicated in Fig. 1(a). Site 8 refers to a C atom site of the nearest neighbors in the adatom. Site 19 refers to the adatom itself. (a) Total DOS. (b) LDOS of one of the C atoms of the six-membered ring, at which a Hf atom is adsorbed on a HOLLOW site. In the upper plot, the red line shows the s orbital. In the lower plot, the red line shows the pₓ orbital, the green line shows the pᵧ orbital, and the blue line shows the p₂ orbital. (c) s and p orbitals of the LDOS of the Hf atom that are adsorbed on the HOLLOW site. In the upper plot, the red line shows the s orbital. In the lower plot, the red line shows the pₓ orbital, the green line shows the pᵧ orbital, and the blue line shows the p₂ orbital. (d) d orbitals of the LDOS of the Hf atom adsorbed on the HOLLOW site. In the upper plot, the green line shows the s orbital. In the middle plot, the blue line shows the dₓ₂−𝑦₂ orbital and the red line shows the d_yz orbital. In the lower plot, the red line shows the d_pₓ orbital and the blue line shows the d_zy orbital.

adsorbed on the HOLLOW or TOP site. We name the three local stable structures “Trimer HOLLOW,” “Trimer TOP void carbon centered,” and “Trimer TOP carbon centered.” Trimer HOLLOW becomes the most stable of the six structures, and the adsorption energy per Hf atom is 5.46 eV. The most unstable of the six structures for a coverage of 0.167 is the Homogeneous BRIDGE structure. The BRIDGE-site adsorption is not very stable in the adatom. These results agree with the results for a coverage of 0.056 and the PES. In the most unstable structure in coverage 0.167, construction made from BRIDGE site adsorption is only Homogeneous BRIDGE. Therefore, for a coverage of 0.167, we can understand when the Homogeneous BRIDGE structure is the most unstable. The Homogeneous HOLLOW structure is the most unstable after the Homogeneous BRIDGE structure. The energy difference between the Homogeneous BRIDGE and other structure is about 1 eV. HOLLOW-site adsorption is the most stable for a coverage of 0.056, but the Homogeneous HOLLOW structure located in the three hollow sites for a coverage of 0.167 is slightly less stable than the other structures. In the structure with a coverage of 0.167, the energy difference is about 0.1 eV, with the exception of the Trimer HOLLOW structure. In other words, the migration energy to other structures is small.

Three local stable structures with a trimer structure exist for a coverage of 0.167. The Trimer HOLLOW structure has two special features: Hf atoms are adsorbed on the hollow site of three six-membered rings and Hf atoms are adsorbed by a trimer-type structure. The “Trimer TOP void carbon centered” structure is adsorbed on the TOP site around the HOLLOW site of one six-membered ring of trimer type. The “Trimer TOP carbon centered” structure is a trimer-type structure in which a Hf atom is adsorbed on three C atoms around one C atom. The Trimer HOLLOW structure is the most stable among these structures. The energy difference between other trimer structures for a coverage of 0.167 is very near 0.1 eV. The PES calculation results (Fig. 3) suggest that the energy difference between the Trimer TOP void carbon centered and Trimer TOP carbon centered structures is very small; this is plausible because the potential energy surfaces of these trimer structures, which have a Hf atom located on each C atom, are almost the same.

Figure 1(d) shows the adsorption results for a coverage of 0.375. For the calculation of adatoms at several sites, the coordinate normal to the surface is fully relaxed. One atom at the edge of the 2 × 2 structure of the graphene sheet is fixed during the relaxation of the other carbon atoms of the sheet. In this result, the structure in which two Hf atoms are adsorbed on the TOP site and one Hf atom is adsorbed on the HOLLOW site becomes stable. This structure is the most stable structure in the coverage range from 0.056 to 0.375. If adsorption of the Hf atom is monoatomic adsorption, HOLLOW-site adsorption is the most stable, but under a high coverage, the Hf atoms are not adsorbed on all HOLLOW sites. The C atom has one pₓ orbital contributing to a bond. The Hf atom has four valence electrons contributing to a bond. The
The bulk of the HCP-Hf [0001] surface is 3.19 ˚A, and the Hf-Hf bond distance is about 3.20 ˚A, and the Hf-Hf bond distance in the [0001] surface of the hcp structure. The Hf-Hf bond length in the 0.375 coverage structures. In other words, this distance is formed when we follow the adsorption site of the Hf atom for 0.375 coverage structures. Interestingly, the most stable adsorption structure for a coverage of 0.375 is hcp-Hf [0001], the same as that of the Hf-Hf bond distance in the bulk of the hcp-Hf [0001] surface is 3.19 A.

HOLLOW-site adsorption bonds to a valence electron of the Hf atom for one six-membered ring. When the coverage factor increases, the number of C valence electrons binding to the Hf atom adsorbing on the HOLLOW site decreases. Furthermore, we notice that a triangular lattice is formed when we follow the adsorption site of the Hf atom for 0.375 coverage structures. In other words, this is the [0001] surface of the hcp structure. The Hf-Hf bond distance is about 3.20 A, and the Hf-Hf bond distance in the bulk of the hcp-Hf [0001] surface is 3.19 A.

FIG. 3: The potential energy surface (PES) when one Hf atom is adsorbed on graphene. Shown is an energy contour map when a Hf atom is adsorbed on various points in the six-membered ring. The Hf atom is made to relax only along the z axis direction and is fixed with respect to the other coordinates. In the PES, we defined the lowest adsorption energy as the origin (=0).

IV. CONCLUSION

The adsorption energy per Hf atom is the largest for a structure of coverage 0.375 when a Hf atom is adsorbed on graphene. When a Hf atom is adsorbed on the HOLLOW site, the adsorption energy tends to increase, and the subsequent metastable adsorption is TOP-site adsorption. BRIDGE-site adsorption is the most unstable, but it is a saddle point with a local stability site. These features are unique to monoatomic adsorption, but the results are similar when coverage is increased. When coverage increases, the adsorption energy per Hf atom increases. The magnetic moment plays almost no role other than in the HOLLOW-site adsorption for a coverage of 0.056. It is well known that the Hf atom does not develop ferromagnetism in the bulk. Therefore, it is easy to understand why the magnetic moment disappears when coverage increases. Because the localization orbital that does not do p_z orbital and a hybrid of the graphene is created on Fermi level in the case of monoatom adsorption, magnetic occurs. In many cases, the d electron of Hf and the s electron do not make a magnetic contribution to a bond. Interestingly, the most stable adsorption structure for a coverage of 0.375 is hcp-Hf [0001], the same as that of the surface. This fact is important as an indicator when Hf and Hf compounds are grown on graphene or a graphite substrate.

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