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# DFT Calculation for Adatom Adsorption on Graphene

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## 1. Introduction

Graphene is well-known to be two-dimensional material made of carbon atoms. Graphene is the basic material to form nanotube, fullerene and graphite. Graphene is a substance that attracts attention not only as parts of the nanocarbons but also for its own interesting electronic and mechanic properties ( T. Ando, A. K. Geim et.al, K.S. Novoselov et.al). In the last decade, the most significant problem is how to make wide and high quality graphene itself. Nowadays, good quality graphene can be made in laboratories, for example, using SiC(0001) surface. Thus, one of the next step of the research related to graphene is how to make nano structures on graphene plane (V. M. Karphan et.al ).

Recently, H.Fujioka et al. has succeeded for the growth of GaN on graphite using PLD (Pulsed Laser Deposition) method and they success to make light emission diode using GaN on graphite (K. Ueno et.al, A. Kobayashi et.al 2006, A. Kobayashi et.al 2007, G. Li et.al, M.-H. Kim et.al, H.Fujioka 2009 ). Since the graphite is made of the stacking of many graphene plane, similar growth will be possible for graphene, if the graphene plane is supported mechanically with the other certain material. Such growth is not limited to GaN, but many other possibilities to form nano structures, nano devices or thin films on graphite plane. In order to apply graphene for such purpose, however, we should first investigate deeply for the interaction between adatoms and graphene plane ( A. Ishii. et.al 2008, K.Nakada et.al). In experiments, the adatom adsorption on graphene is reported for some atomic species (I. Zanella et.a, K. Kong et.al, K. Okazaki et.al, A. Lugo-Solis et.al, M. Wu et.al, H.Gao et.al, J. Dai et.al ) , but not for all atomic species.

In this chapter, we introduce the adsorption mechanism, atomic structures, stability, migration barrier energies and electronic properties of the adatom adsorption system on graphene plane for most all atomic species using the density functional theory. First, we review briefly the basic properties of graphene used in the following sections as remarks. The band structure of graphene is shown in figure 1. Because of the in-plane hexagonal symmetry, the  $p_x$  and  $p_y$  orbitals are degenerated. The  $s$ -orbital and the degenerated  $p_x$  and  $p_y$  orbitals make  $sp^2$  hybrid orbitals in the graphene plane as  $\sigma$  bonds. The  $p_z$  orbitals are out of the  $sp^2$  hybrid orbitals and they form the  $\pi$  bonds normal to the graphene plane. These  $p_z$  orbitals forms bonding orbital ( $\pi$ ) and anti-bonding orbital ( $\pi^*$ ) below and above the Fermi

energy level. These two bands have no bandgap and they contact at one point in the momentum space just at the Fermi energy.

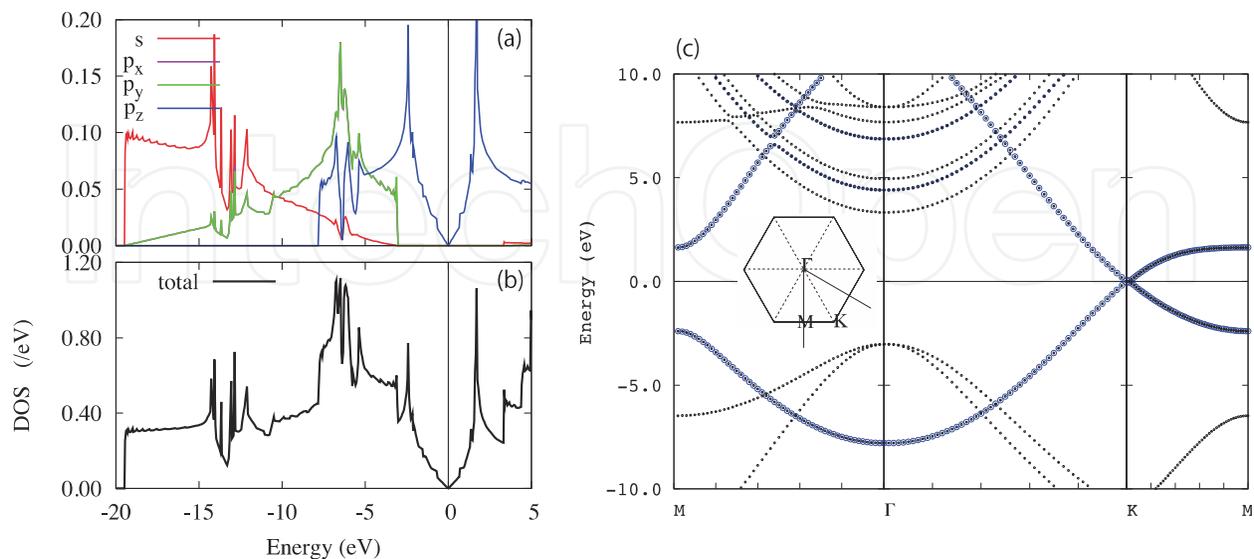


Fig. 1. (a) Local density of states projected to  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$  orbitals for graphene. (b) Total local density of states for graphene. The LDOS projected to  $p_x$  and  $p_y$  are degenerated. (c) Band structure of  $1 \times 1$  graphene. The blue lines in the figure correspond to wave functions of  $p_z$  orbitals.

Near the point, the band is linear so that the effective mass of the electron of the bands are zero. This point is known to be "Dirac point", because the band structure around the point is similar to the massless Dirac particle as the solution of the Dirac equation of the relativistic quantum mechanics. The Dirac point is very important in the physics of graphene. Because of this feature, the mobility of electron in graphene is very large. The theoretical prediction of the mobility is 1000 times larger than silicon and experimentally observed mobility is more than 100 times, at least. This large electron mobility is one of the significant reason that the graphene is expected to be the material of the future nano device. Using the large mobility, we can expect a lot of application for graphene for small gate voltage for electrons and holes of the device. Moreover, interesting features of graphene are large heat conductivity, large Young's modulus and light weight because of carbon atoms. Because of the two-dimensionality of graphene, adsorption of atoms or molecules on graphene affects the electronic properties of graphene itself dominantly through the  $p_z$ -orbitals. It means that the doping effect for graphene is very interesting.

## 2. Calculation method

In this work, we used a first-principles band calculation technique based on density functional theory. We used VASP (G.Kresse et.al 1993, G.Kresse 1993, G. Kresse et.al 1996, G. Kresse et.al 1996 ) which is a first-principles calculation code with high precision using the PAW method (G. Kresse and D. Joubert ). We adopted LDA ( P. Hohenberg and W. Kohn, W. Kohn and L. J. Sham ) as the term exchange correlation with a cutoff energy of 500 eV and all calculations performed nonmagnetically. The unit cell for the graphene sheet adopted a  $3 \times 3$  structure. The lattice constant of the graphene used the value optimized by

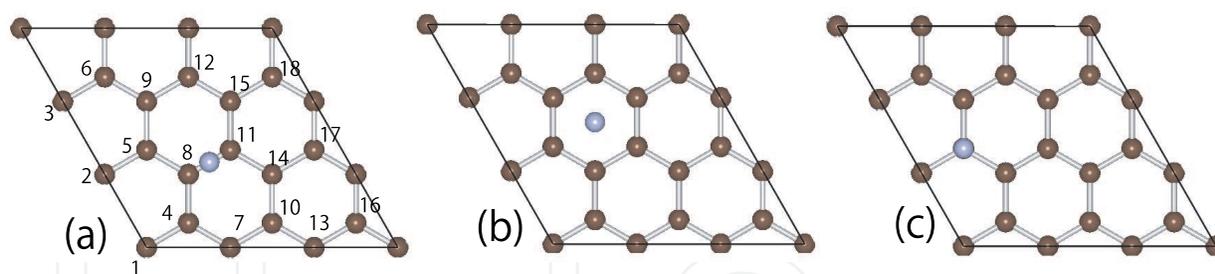


Fig. 2. Adsorption sites of graphene of  $3 \times 3$  supercell. (a) Bridge site (B-site) positioned at the center of C-C bond. Number in the figure shows us the numbering of each carbon atoms of the  $3 \times 3$  supercell. (b) Hexagonal site (H-site) positioned at the center of the six membered ring. (c) Ontop site or tetrahedral site (T-site)

calculation. The distance between graphene sheets is about  $14.7\text{\AA}$  and the distance between adatoms is about  $7.3\text{\AA}$ . The final potential is constructed self-consistently from eigenstates at 24 sampling k-points in the irreducible Brillouin zone (IBZ). For the calculation of adatoms at certain sites, the position coordinate of the adatom parallel to the surface is fixed and the coordinate normal to the surface is fully relaxed. One atom of 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. Using the coordinate which converged potential, we performed convergent calculation using 240 k-sampling point in the IBZ. To obtain a final potential, we calculated a  $3 \times 3$  graphene. Fig.3 is band structure and BZ of  $3 \times 3$  graphene. Owing to the supercell used in the calculations, the K point of the  $1 \times 1$  graphene BZ in Fig.1(c) is folded into the  $\Gamma$  point of the supercell BZ. Similarly, the M point of the  $1 \times 1$  graphene BZ is foled into the  $\Gamma$  of the supercell BZ. We calculated supercell BZ with M- $\Gamma$ -K-M line to follow the dispersion of the Dirac point. The calculation was carried out at three adsorption sites, H, B and T shown in Fig. 1. We calculated the adsorption energy from the formula

$$E_{\text{bond}} = (E_{\text{graphene}} + E_{\text{adatom}} - E_{\text{total}}). \quad (1)$$

$E_{\text{bond}}$  is the binding energy of the adsorbed atom to the graphene sheet.  $E_{\text{graphene}}$  is the total energy of one sheet of the graphene and  $E_{\text{adatom}}$  is the total energy as an isolated atom of the adatom. We treated almost all the elements of the periodic table except the lanthanoids and noble gases as adatoms and carried out the calculation from H to Bi.

### 3. Result and discussion

#### 3.1 Adsorption energy

The 3d transition metal is spin polarized at low temperature. In some groups (K. T. Chan et.al, P. A. Khomyakov et.al), calculations considering spin polarization are performed for a few adatoms. However, if the nonmagnetic state is one of the ground state, its calculation is as important as the spin polarization calculation. In other words, the nonmagnetic state is in the condition to take an average of the spin, and it is the starting point for discussion of the ferromagnetic state and the discussion of high temperature. As the first step in the discussion of the growth of a compound semiconductor on graphene, we discuss the electronic state in the nonmagnetic state. Fig. 4 is the calculation result for the nonmagnetic state. This figure shows the most stable adsorption site and bond energy when various adatoms are adsorbed at three adsorption sites. In the figure, the most stable sites for each adatom are indicated by colors. The green, red and yellow boxes mean that the most stable

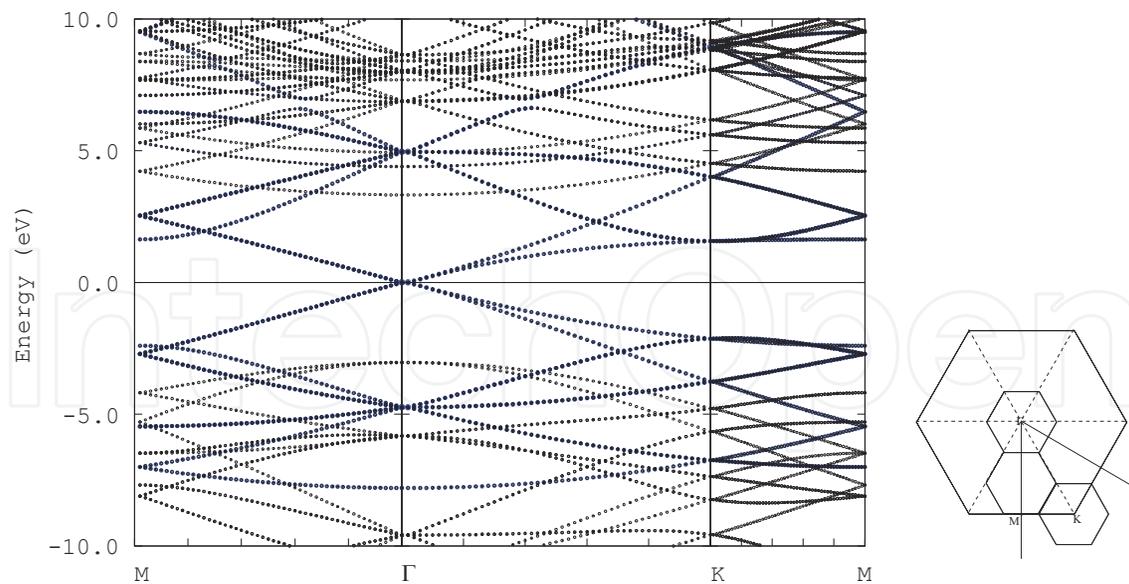


Fig. 3. The band structure and BZ of  $3 \times 3$  graphene. The blue lines in the figure correspond to wave functions of  $p_z$ -orbitals.

site is the B-site, H-site or T-site respectively. The value in Fig. 4 shows the magnitude of the adsorption energy when each adatom is adsorbed to the most stable adsorption site. This result shows that for the transition metal elements the most commonly stable is the H-site. For the nonmetallic elements, the B-site is most stable. For H, F, Cl, Br and I, where the valence electron number of the adatom is 1, the T-site is the most stable adsorption site. In addition, for transition metal elements, the magnitude of the adsorption energy of each adatom is very large. The largest adsorption energy is shown for the adatoms of the nonmetallic elements C, N, O. For the transition metal elements, the bond energy shows an increasing tendency with an increasing number of d-electrons. Furthermore, it shows a tendency for the bond energy to decrease when the number of d-electrons increases to more than half occupancy, because the d-orbitals are shifted down. Therefore we find very large bond energy for Mn, where the d-orbital is half occupied. The bond energy is a very large on metal element adsorption, but this state is unstable because it is constructed from a localized non-bonding band at the Fermi level and the number density of states at the Fermi level ( $DOS(E_F)$ ) is very large. There is low bond energy for Cu, Ag, Au because all d-orbitals are occupied. Furthermore, the bond energy becomes very small for Zn, Cd, and Hg, where the s-orbital is close to the d-orbital. In addition, there is almost no difference in the adsorption energy of the three adsorption sites when the adsorption energy of the adatom is small. In contrast, the adsorption energy is large for the nonmetallic elements C, N, O and the difference of adsorption energy between sites is also large (higher than 3.0 eV). This shows it to be easy to adhere strongly to the B-site. However, there are a few differences between the adsorption energy of the T-site and the B-site when the adatom is C. Fig. 5 is a table of the bond distance between graphene and the adatom. ("The bond distance" means the distance between the average of the position of the graphene sheet and the adatom.) In the case that the bond distance between the adatom and graphene is large, the binding energy tends to reduce. In the case of a large bond distance, the adatom shows physical adsorption-like bonding. When the bond distance is short, the bond energy tends to increase. In this case the bonding feature is like chemical adsorption.



metal, transition metal and the calculation which adsorbed the nonmetallic element. The (a)-(p) in fig.7 corresponds to K,Ca,Se,Ti,V,Cr,Mn,Fe,Co,Ni,Cu,Zn,Ga,Ge,As and Se adsorption.

H																	He
1.49																	
Li	Be											B	C	N	O	F	Ne
1.62	2.93											1.72	1.65	1.62	1.59	1.87	
Na	Mg											Al	Si	P	S	Cl	Ar
2.22	3.21											2.04	2.03	2.09	2.08	2.56	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2.58	2.14	1.76	1.56	1.47	1.42	1.38	1.38	1.42	1.47	2.03	3.02	2.11	2.16	2.22	2.25	2.78	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
2.74	2.37	2.00	1.74	1.66	1.59	1.57	1.62	1.71	2.08	2.42	3.18	2.35	2.42	2.46	2.49	3.26	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
2.84	2.49	2.07	1.85	1.65	1.60	1.58	1.61	1.70	2.12	2.41	3.13	2.48	2.53	2.57			

Fig. 5. Distance between the adatom and graphene in the most stable adsorption site: a red substrat shows distances less than  $2\text{\AA}$ , a white substrate shows distances more than  $2\text{\AA}$ .

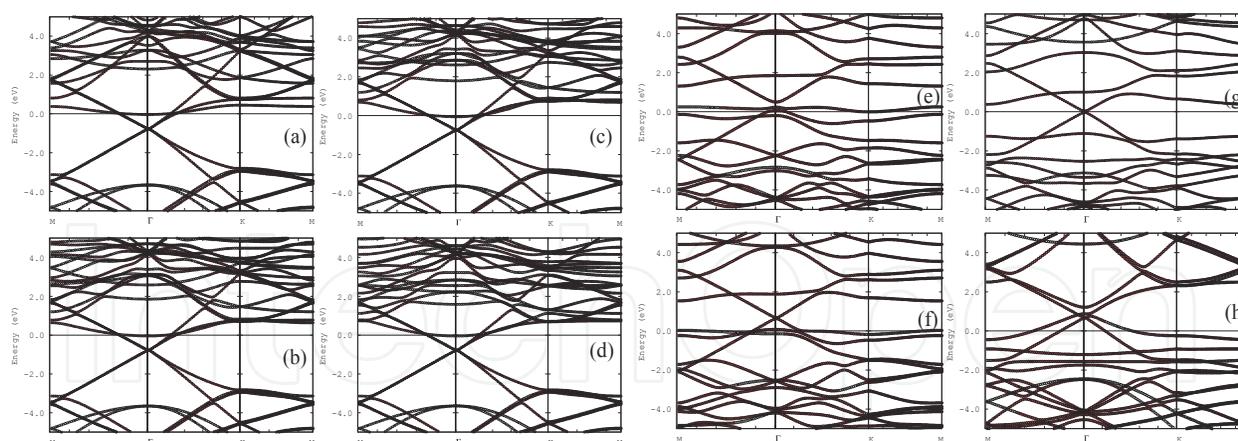


Fig. 6. Typical example for physical and chemical adsorption. A red circles correspond to the amount of adatom of  $p_z$  character. The adatom is (a) Na, (b) K, (c) Ru, (d) Cs, (e) C, (f) N (g) O and (h) F.

The left axis of fig. 6 shows density of states (/eV), and the right axis shows local density of state of adatom (/eV). It is performed a projection of a wave function of the adatom to s,p,d orbital. The wave function character is calculated, either by projecting the orbitals onto spherical harmonics that are non-zero within spheres of a radius. Each calculation is result of the H-site adsorption. In a model metallic element and the transition metal element, H

site adsorption is most stable. B-site adsorption is most stable in the metalloids such as Ge, As and Br, but shows calculation result of the H-site adsorption for comparison. 18 C atoms constituting graphene is included in the  $3 \times 3$  unit cell. We change an axial contraction scale of LDOS to compare LDOS of the adatom with the DOS of the total. As for the K adatom adsorption on the graphene in figure 7(a), peak structure of the p-orbital appears around 12eV. The 3p-orbital of the K atom is a closed shell, but it is necessary to treat 3p-orbital as a valence electron because there is the orbital in a shallow rank. In other words, we prepared for pseudopotential to treat 3p-orbital as a valence electron to treat it as shallow core. Almost of 3p bands are lone status, but hybridization with the graphene is slightly shown. The 3d-orbital is not occupied with an electron. Conduction band constructed from 3d is fermi level upper 5eV. In the K and the Ca atomic adsorption, the 3d-orbital is located in the conduction electron band of the Fermi surface upper part. However, the valence band around the Fermi level is occupied by d-orbital of the adatom when we adsorbed adatom from Sc to Cu. One of the reasons of strong energy when transition metal was adsorbed is a hybridized orbital between 3d-orbital of adatom and p orbital of graphene. The peak structure is located around the Fermi level. The peak structure around the Fermi level is made from the wave function of adatom which does not hybridize orbital. In figure 8, for typical example, we show a band structure of the Cr atomic adsorption on the graphene with high adsorption energy. Fig. 8 shows a band structure close to the Fermi level when a Cr atom adsorbed to the graphene B-site, H-site and T-site. The wave function projected to  $p_z$  orbital in the 8-site of C atom is plotted in blue color circle. The most stable adsorption site is H-site. The  $\pi$  bonding bands made from the  $p_z$  orbital of the graphene is broken by B-site adsorption and the T-site adsorption. However, the  $\pi$  bonding band is kept when a Cr atom adsorbs on the H-site. The wave function projected to  $p_z$  orbital in the 8-site of C atom is plotted in blue color circle. The adatom was adsorbed each in (a) the B-site, (b) the H-site and (c) the B site. We can understand from a surface structure (Fig. 9) of the graphene after the Cr atomic adsorption. The Figure 9(a) is a side view of the graphene structure when a Cr atom adsorbed on the B-site. When adatom adsorbed H-site, we showed it in figure 9(b) and showed it to figure 9(c) when we adsorbed T-site. When adatom adsorbs on the B-site and the T-site, a structure of the graphene after the adsorption is warped. However, a structure of the graphene does not change when adatom adsorbs on the H site. In other words a  $\pi$  bonding band of the  $p_z$  orbital of the graphene functions enough because symmetry of the graphene does not collapse when adatom adsorbs in the H-site. Almost all H-site adsorption is most stable in the adsorption of the transition metal in many cases. When adatom adsorbs on the H-site ( the center of the six-membered ring ), a lot of adjacent bond between adatom and the C atom is made. However, when adatom adsorbs on the B site and the T-site, bonding between the specific C atom and adatom becomes strong, but bonding with the other C atom becomes weak. Besides,  $\pi$  bonding is made weak when adatom adsorbs on the H-site and the T-site because a surface structure of the graphene is broken. Figure 10 drew the wave function ( charge density map ) of the band of around the Fermi level when a Cr atom adsorbed to the graphene. In fig. 10, A charge density map when a Cr atom adsorbed to the graphene. (a-1) and (a-2) show a charge density map made from around fermi the 39th band from the bottom. A shape of typical  $d_{3z^2-r^2}$  -orbital is shown in the 39th band. We can understand that 39th band is very

localized by comparing fig. 7(f) with fig.10(a). The p-d orbital hybridization of C atom and the adatom begins with a band than 37th band below.

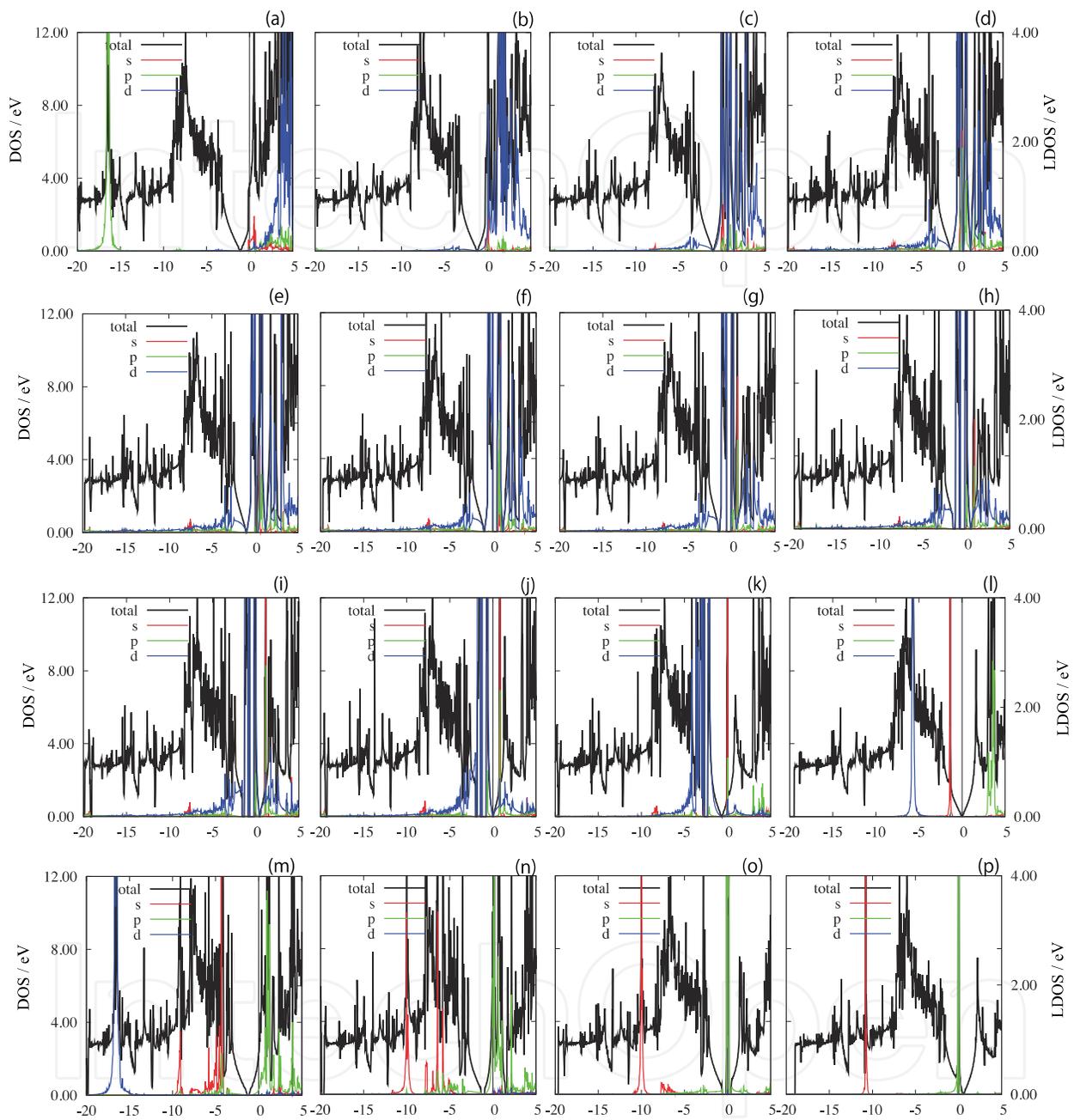


Fig. 7. Density of states of the fourth period and local density of state. There is no spin polarization. A black line is density of states, and the value is shown in a left axis. The local density of state of the adatom is shown with axis of the right side. Local density of states projected to s, p, d orbitals for graphene. A red line shows s orbital, a green line shows p orbital, and blue line shows d-orbital component. (a)-(p) is the calculation result which adsorbed K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As and Se atom on graphene.

In Fig.7, we follow a band located very much just under the fermi level. In fig. 7, a band structure of the Cr, Mn, Fe, Co and Ni atomic adsorption which is 3d transition metal element is illustrated. These very localized around fermi level and the number of the density of

status is very large. In addition, the  $\pi$  band of the graphene is divided by localized d-orbital. The number of the very large status just under the fermi level shows that status is instability.

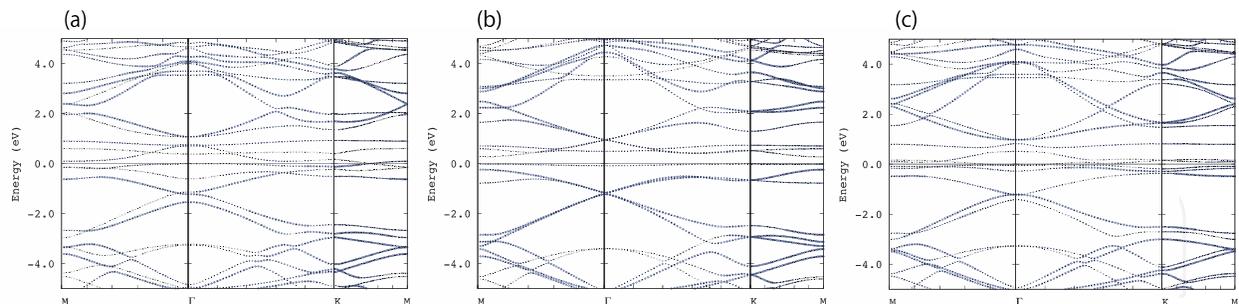


Fig. 8. A figure of band when Cr adatom adsorbed in each adsorption site in the graphene. The wave function projected to  $p_z$ -orbital in the 8-site of C atom is plotted in blue color circle. The adatom was adsorbed each in (a) the B-site, (b) the H-site and (c) T-site.

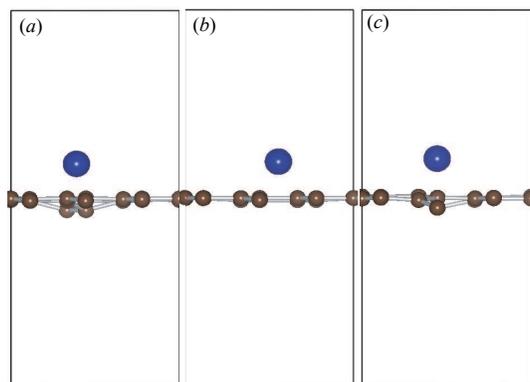


Fig. 9. A surface structure when a Cr atom adsorbed in each adsorption site in the graphene. (a) B-site, (b) H-site, (c) T-site.

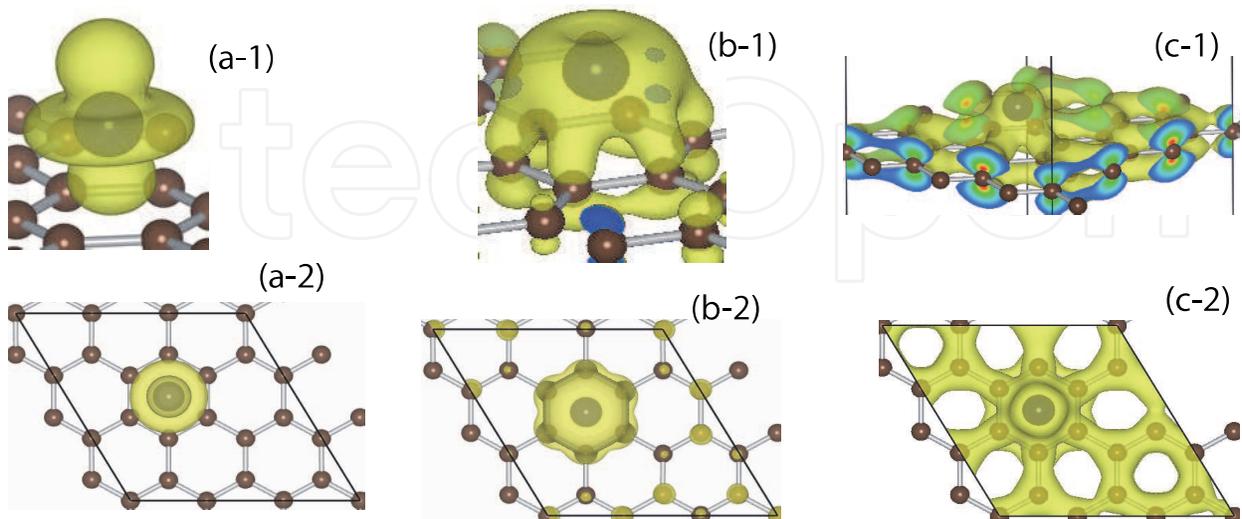


Fig. 10. A charge density map when a Cr atom adsorbed to the graphene. (a-1) and (a-2) show a charge density map made from the 39th band from the bottom. (b-1) and (b-2) is made from 37th band. (c-1) and (c-2) is made from 35th band.

We performed all nonmagnetic (we do not consider spin polarization) calculation. In other words, this shows that status is stabilized by spin polarization. In figure 11, we show calculation result in consideration of spin polarization of the 3d transition metal Ti, V, Cr, Mn, Fe, Co and Ni. A left axis shows total density of states (/eV) in the figure, and the right axis shows local density of state (/eV) of the adatom. The local density of state of the graphene does not almost influence polarization. Only 3d electron of the adatom and C atom around the Fermi surface cause polarization. We plotted only 5eV from -5eV around the Fermi level in fig. 11. In fig. 12, a calculation in consideration of spin polarization. A black line is density of states, and the value is shown in a left axis. The local density of state of the adatom is shown with axis of the right side. Local density of states projected to s, p, d orbitals for graphene. A red line shows s orbital, a green line shows p orbital, and blue line shows d-orbital component. (a)-(g) is the calculation result which adsorbed Ti, V, Cr, Mn, Fe, Co and Ni atom on graphene.

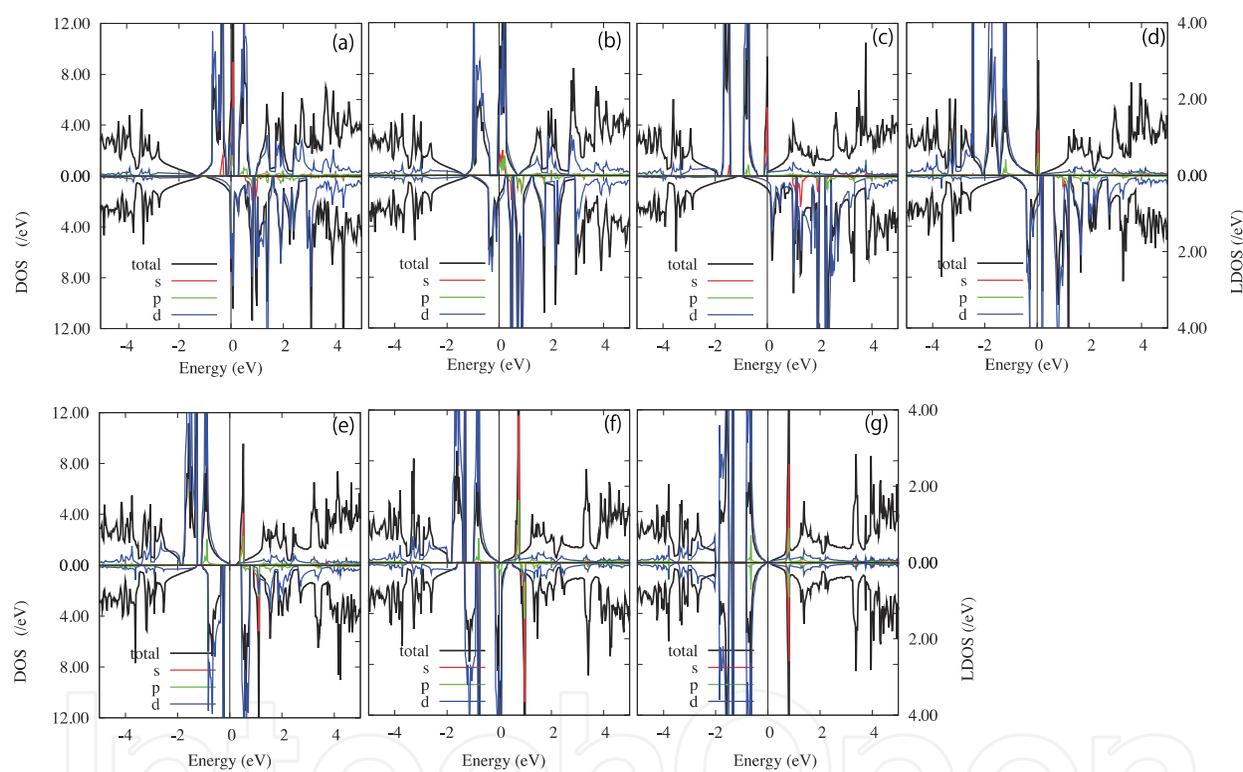


Fig. 11. Calculation in consideration of spin polarization. A black line is density of states, and the value is shown in a left axis. The local density of state of the adatom is shown with axis of the right side. Local density of states projected to s, p, d orbitals for graphene. A red line shows s orbital, a green line shows p orbital, and blue line shows d orbital component. (a)-(g) is the calculation result which adsorbed Ti, V, Cr, Mn, Fe, Co and Ni atom on graphene.

For the calculation in consideration of spin polarization, the case which the adsorption energy shows most high value when a Ti atom adsorbed, Fe atom adsorbed shows the second largest value. Migration energy is maximum the case which a Fe atom adsorbs, the case which a Ti atom adsorbs shows the second largest migration energy. The stable adsorption site is not different from spin polarization in calculation without the spin polarization. The adsorption energy decreases in comparison with the result that does not consider spin polarization widely generally. A tendency to decrease is seen in the

adsorption energy in comparison with the result that does not consider spin polarization. Most of the difference of the adsorption energy are because total energy (formula 1) of the isolated atom is different by spin polarization. By the total energy of the 3d transition metal isolated atom by spin polarization of number eV make a great difference. In other words, originally the adsorption energy showed a slight overestimate for the calculation that did not consider spin polarization. The large difference by the spin polarization is a change of the migration energy. In other words, for the calculation in consideration of spin polarization, the energy difference between adsorption sites decreases. When specially spin polarization is large, we appear conspicuously. When spin polarization is large, it is remarkable. When a Cr atom adsorbs, the exchange splitting with the spin is the largest ( $4 \mu_B$  / adatom ). In this case the energy seems to profit by exchange splitting, but the adsorption energy is small because most of the orbital hybridization with the graphene does not exist. In the graphene adsorption of the Mn atom, similar discussion is possible. However, except such a case, magnitude and the tendency of the adsorption energy in the most stable adsorption site are about the same as a result of nonmagnetism. The difference of the migration energy by the spin polarization needs attention in the 3d transition metal.

adatom	migration	B-site	H-site	T-site	moment
Ti	0.78	1.76	2.55	1.77	1.65
V	0.45	1.46	1.91	1.41	1.36
Cr	0.12	0.65	0.77	0.65	4.16
Mn	0.14	-0.01	0.26	0.12	0.78
Fe	1.06	1.20	2.31	1.25	1.86
Co	0.73	1.88	2.61	1.83	0.92
Ni	0.43	2.22	2.65	2.17	0.00

Table 1. A calculation result when the 3d transition metal adatom which considered spin polarization adsorbed to the graphene. We show migration energy when we adsorbed to the H site of the most stable adsorption site. When adatom adsorbed each to the B,H,T sites, we show adsorption energy and magnetic moment. The magnetic moment shows magnetic moment per adatom ( $/\mu_B$ ).

### 3.2 Migration energy

In the above section, we discuss the adsorption energy for adatoms on graphene plane. The adsorption energy is the energy to remove the adatom from the graphene. Here, we discuss the other important energy, migration energy. Migration energy or migration barrier energy is the required energy for adatom on graphene to move from a site to other site. For the case of large migration energy, adatom does not move at room temperature. For the case of small migration energy, adatom can move easily on the graphene plane even at room temperature.

In general, for making nano structures on a surface, the migration barrier energy for the adatom on the surface is very significant to discuss the temperature dependence of the nano structure. For adatom having small migration energy, the nano structure on the surface can easily disappear because of the movement of the adatoms on the surface. For the growth of thin films on surface using epitaxy technique, the choice of the growth temperature is very important, because adatoms to form the thin film should move on the surface. Thus, the growth temperature is a function of migration energy of the adatom on the surface.

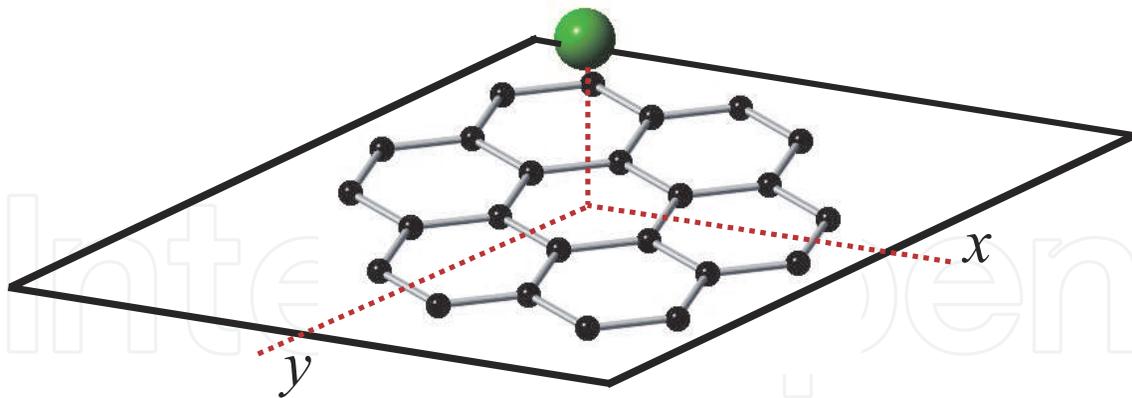


Fig. 12. A sketch of the migration energy. Migration energy or migration barrier energy is the required energy for adatom on graphene to move from a site to other site.

In figure 13, we show the table of the calculated migration energies for various adatoms on graphene. From the result, we found that adatom can be distinguished into two groups; adatoms with fixed adsorption site and mobile adatoms. Roughly speaking, the two groups are separated at the migration energy value of 0.5 eV. Above 0.5eV, adatom does not move at room temperature. Below 0.5eV, adatom is very mobile even at room temperature.

$$R = R_0 \exp(-E / k_B T)$$

The rate of hopping of adatom per second,  $R$  can be expressed with the above formula, where  $E$  is the migration energy,  $T$  is temperature and  $k_B$  is the Boltzmann constant.  $R_0$  is a prefactor. The prefactor for Si adatom on Si(001) surface, the value is determined to be  $1.25 \times 10^{10}$  (T.Kawamura et.al). If we consider the graphene plane having more than 1 million atoms, the migration barrier energy 0.5eV corresponds to the hopping of at least one atom within one second. For example, Ito and Shiraishi have reported a kMC simulation of MBE which takes into account the electron counting model (T. Ito et.al, K.Shiraishi et.al). They have used parameters such as the hopping barrier energies obtained by first-principles calculation. The migration barrier energy can be obtained by using the density functional method where the barrier energy can be easily found by using the contour map of the total energy of the adatom-graphene system as a function of the position of the adatom parallel to the graphene plane. As a beginning Ito and Shiraishi, migration barrier energies of an adatom on surface has been calculated by many researchers using the density functional theory.

According to our calculation, the migration barrier energies of adatom on graphene can be distinguished into two types; fixed adatom and mobile adatom. For some transition metals, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, Tc, Ru, Ta, W, Re, Os, the migration barrier energy at the most stable site is very large so that these atoms adsorb on graphene strongly and do not move on graphene plane. On the contrary, for many atoms, Be, B, Na, Mg, Si, Cl, K, Ca, Cu, Zn, Ga, Ge, Br, Rb, Sr, Y, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, Ir, Pt, Au, Hg, Tl, Pb, Bi, the migration barrier energies are very small so that these adatoms can move even at room temperature.

The 3d transition metal is polarized with low temperature. Our calculation was carried out without magnetism. However, the nonmagnetic calculation is the calculation that becomes average about a spin. It is the starting point for the discussion of the ferromagnetic state and the discussion of high temperature. For a typical example, by calculating the Ti adatom

adsorption on graphene, a discussion of the metal-graphene junction is carried out [18–21], because the Ti atom has a very large adsorption energy and large migration energy. Furthermore, an important fact is that the Ti atom does not break the structure of graphene on adsorption. Fig. 15 shows a structure of the graphene adsorption of the Ti atom using a nonmagnetic calculation. The adatom disturbs the structure of graphene on adsorption at the B-site and the T-site. However, there is no change of the graphene structure from H-site adsorption. The H-site is the most stable adsorption site for Ti adsorption. It is important for the growth of a compound semiconductor on graphene that the adatom does not disturb the surface structure. In table 1, we performed a calculation including spin polarization for a adatom of 3d transition metal. As a result, the structure does not change with the H-site adsorption, just as for the nonmagnetic calculation. The adsorption energy decreases, but it is energy very larger than physical adsorption. For our calculation, the adsorption energy is 2.55 eV when including the spin polarization. The migration energy is very high then with 0.78eV. When a Ti atom adsorbs on graphene, it is result almost same as nonmagnetism. However, the migration energy is lower than nonmagnetic result in the 3d transition metal adsorption. The adatom which is over threshold sill level 0.5eV of the migration energy at the room temperature is only Ti,V,Fe and Co in the 3d transition metal. One of the reasons which Ti atom is used for in metal-graphene junction is caused by migration energy and adsorption energy.

H																	He
0.60																	
Li	Be											B	C	N	O	F	Ne
0.30	0.02											0.12	0.25	1.00	1.02	0.45	
Na	Mg											Al	Si	P	S	Cl	Ar
0.13	0.02											0.05	0.05	0.45	0.46	0.02	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.12	0.07	0.34	0.61	1.05	1.45	1.26	0.97	0.77	0.40	0.03	0.02	0.03	0.07	0.20	0.23	0.00	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.09	0.04	0.12	0.39	0.83	1.47	1.40	0.96	0.39	0.06	0.01	0.01	0.02	0.03	0.03	0.09	0.00	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
0.10	0.05	0.18	0.23	0.60	1.17	1.23	0.75	0.15	0.19	0.03	0.01	0.00	0.01	0.00			

Legend:  
 more than 0.50 eV  
 under 0.50 eV more than 0.30 eV  
 less than 0.30 eV

Fig. 13. The most stable site of migration energy. A dark green color is more than 0.5 eV and a light green color is under 0.5 eV but more than 0.3 eV.

### 3.3 Charge transfer

Charge density analysis are done using AIM method or Bader method (R. F. W. Bader, W. Tang et.al, E. Sanville et.al, G. Henkelman et.al ). In contrast to the Mulliken method using local basis, we use only spacial gradient of charge density to analyze charge density of each atoms using Bader method. Since requiered data is only charge density, we can apply the Bader method in the density functional calculation with the plane wave expansion like

VASP. In fig.15, we show the results the adatom adsorption at the most stable site. The values in the table are the difference of the number of valence electron and the calculated results with Bader method for each adatoms. The value obtained with the Bader method and that obtained with the Mulliken method is usually not equal. No one know which is correct. Nevertheless, we can discuss the charge transfer between adoms using the Bader method calculation where we obtain electron charge density in a certain volume around each atoms. The boundary of each atoms are determined simply as the minimum point of the electron charge density between each two atoms. Therefore, positive values in the table mean that electron transfer from the adatom to the graphene. On the other hand, negative values in the table mean that the electron transfer from the graphene to the adatom.

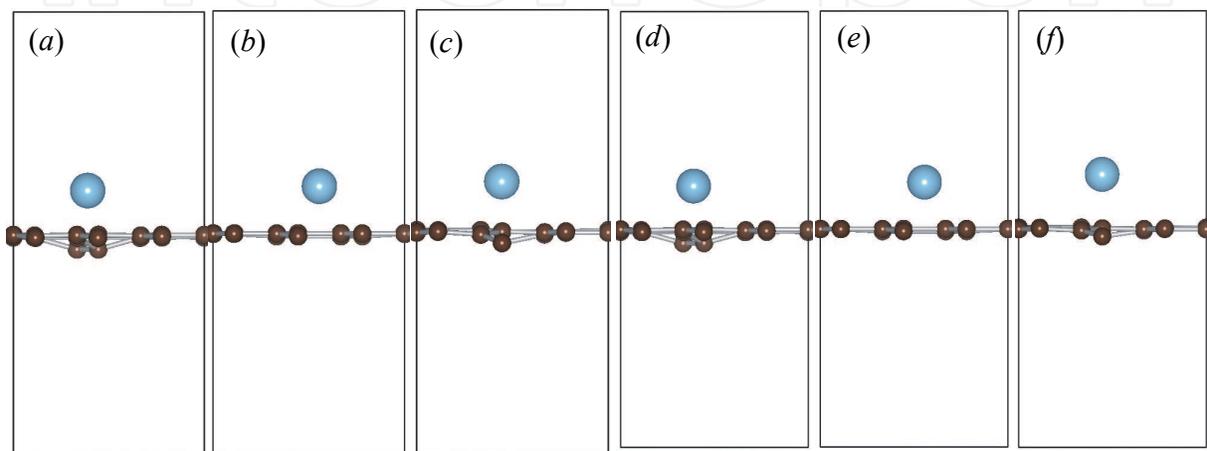


Fig. 14. We showed the final structure for the calculation in the Ti adatom adsorbed the graphene. The calculation that (a)-(b) does not consider spin polarization. The calculation that (d)-(f) considered spin polarization. We show B-site, H-site, T-site adsorption each. The adatom disturbs the structure of graphene with B-site and T-site adsorption. The structure of graphene does not change with H-site adsorption.

The present calculation is the calculation of the charge transfer for the system of one adatom on a graphene plane. Thus, the calculation is almost equal to the study of electronegativity for each adatom on graphene. The feature of our calculation is similar to the general discussion of the electronegativity for each atomic species. For example, non metal atomic species collect electrons from graphene. On the contrary, metallic atom leaves electron to graphene. For some metals, Cu, Ag, Au, or Z, Cd, Hg, we found no electron transfer. Similarly, we found no electron transfer for Pt on graphene, also. These results can be applied for doping to graphene. We show the calculated density of states and the local density of states for non metal species, B, C, N and O adsorbed on graphene in fig.16 (a), (b), (c) and (d). The most stable adsorption sites for the four adatoms are B-site. For Boron, the adsorption energy is 1.8eV and the electrons transfers from B atom to graphene. For Oxygen, the adsorption energy is 4.8eV and the electrons transfers from graphene to the Oxygen adatom. We analyze the local density of states when adsorbed O and B on graphene. We represent typical example of low bond energy at nonmetallic element, in fig. 16(a), adsorbed B. The value of the total density of state corresponds to the left axis. The value of the local density of states of adatom. We plotted the total density of states and local density of states when adsorbed adatom B. This result shows decrease of the local density of state of the adatom in fig 16(a-1) and increase of the local density of states of the graphene in fig. 16(a-2). This result means that charge is transferred to graphene

H	Electron transfer from graphene to adatom																He
0.15																	
Li	Be											B	C	N	O	F	Ne
0.86	0.05											0.43	0.02	-0.68	-0.84	-0.59	
Na	Mg											Al	Si	P	S	Cl	Ar
0.62	0.10											0.81	0.72	0.38	-0.04	-0.41	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.63	0.87	1.1	1.1	0.98	0.84	0.70	0.58	0.48	0.45	0.19	0.03	0.55	0.43	0.22	-0.01	-0.34	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.60	0.82	1.04	1.16	0.97	0.72	0.53	0.37	0.24	0.17	0.10	0.03	0.57	0.43	0.27	0.09	-0.28	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			
0.61	0.86	1.23	0.82	0.83	0.72	0.48	0.35	0.22	-0.00	-0.11	0.01	0.48	0.37	0.24			

Fig. 15. Charge density analysis of Bader. The inserted figure represents the three adsorption sites of graphene sheet, T,B and H. The pinkness signifies electron transfer from graphene to adatom. The green and white signifies electron transfer from adatom to graphene. As for the green, an electron number is larger than 0.5. As for the white, an electron number is less then 0.4.

from adatom when adsorbed B. As a result, the bonding orbitals between adatom and the graphene decrease, because valence electron is transferred from adatom to graphene. Furthermore, we show typical example of high bond energy at nonmetallic element, in fig 16(d), adsorbed O. The value of the total density of state corresponds to the left axis. The value of the local density of states of adatom. This result shows increase of the local density of states of the adatom in fig. 16(d-1) and decreasing of the local density of states of the graphene, in fig16(d-2). The electron of the graphene is transferred to adatom by adsorbing O, as a result, it is made a very wide hybridized orbital between things of graphene and adatom. The cause of strong bond energy when adsorbed O on graphene is a wide hybridized orbital. By the result of the Bader analysis in figure 15, 0.84 electrons per unit cell are transferred to adatom from graphene in the O atomic adsorption, and 0.4 electrons transferred from adatom to graphene in the B atomic adsorption. As well as result from analysis of the density of states, tendency of the charge transfer when we adsorbed O and B was shown from result of the charge density analysis of Bader. We performed Bader analysis about all adatom and the density of states analysis about some atom. The transference of the charge is important to discussion of the bonding of adatom and the graphene. For example, the quantity of charge transfer is important as not only the discussion of the mechanism but also an indicator when it is decided experimentally of the adatom. The results will be very helpful to plan the construction of nano structures on graphene.

## 4. Application

### 4.1 Electrode

The metal-graphene junction attracts much attention for designs such as nano devices and transistors using graphene. When the metal is used as an electrode on graphene, high understand from these results that Ti and Zr bond well with graphene and could be useful as

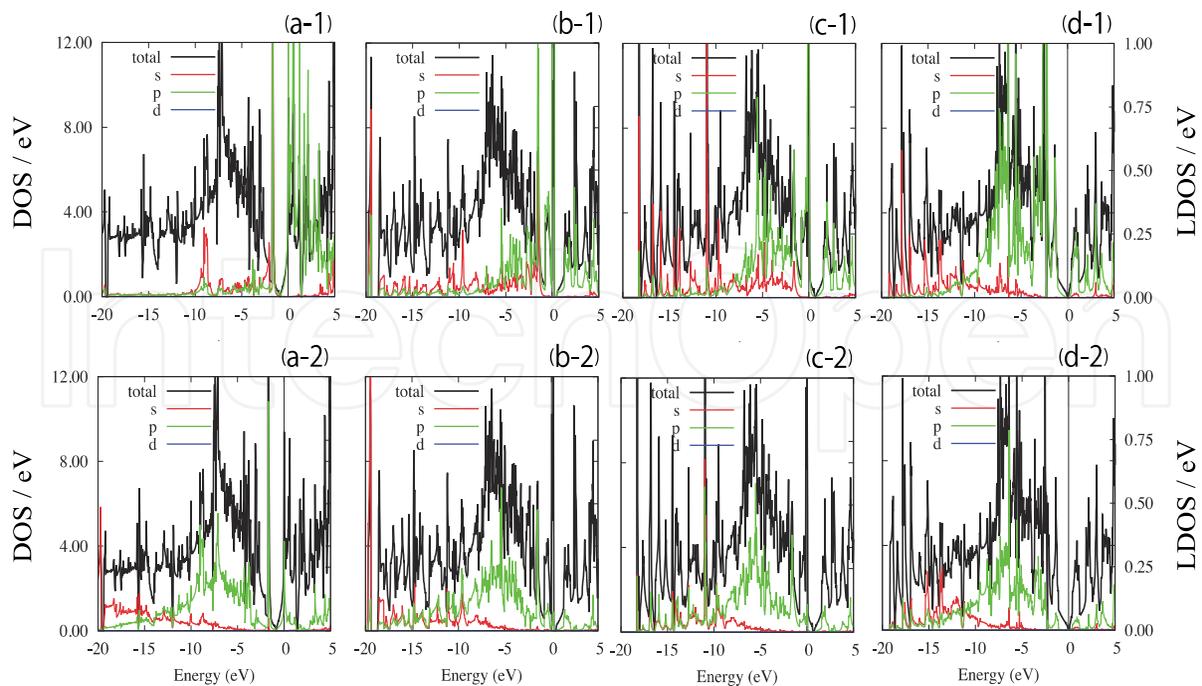


Fig. 16. The density of states and local density of state which adsorbed B,C,N and O. The value of the total density of state corresponds to the left axis. The value of the local density of states of adatom. : As for the black line, total density of states when adatom adsorbed to graphene. A red line shows s-orbital, a green line shows p-orbital, and blue line shows d-orbital component. Local density of states projected to s, p, d orbitals for graphene. (a-1) - (d-1) show local density of state of the adatom. (a-2) - (d-2) shows local density of states of the graphene (11th-site).

adsorption energy and a high migration energy are required, because an adatom is transferred if the migration energy is low at room temperature. Therefore, high migration energy is necessary for the electrode material. Before discussing the electric conduction properties or the work function for various graphene-metal junction to design the electrode material, however, we should discuss the possibilities of electrode materials from the point of view of the migration and adsorption energy as a first step towards that purpose in these studies. In previous studies (K. T. Chan et.al, P.A. Khomyakov et.al, H. Sevincli et.al, Y. Sanchez-Paisal et.al ), the bonding of Ti and Zr on graphene has been discussed. We can see why Ti and Zr attract attention as electrode materials from our calculation, because both the adsorption energy and migration energy are high and they do not disturb the surface structure on adsorption. For our calculation, we found many adatoms with high adsorption energy and high migration energy, similar to Ti and Zr. For example, Mn and Cr atom adsorption have very high adsorption energy and migration energy. However, with the calculation including spin polarization, the adsorption energy decreases in these atom. In Mn adatom adsorption, the adsorption energy is 3.3 eV for the nonmagnetic calculation, but decreases to 0.3 eV when considering spin polarization, because the state of the isolated atom is greatly stabilized by including spin polarization. As regards the state of an isolated atom of a 3d metal, the approximation of an average about spin is not appropriate at low temperature. However, for the adsorption of Ti and Zr adatoms, the adsorption energy and migration energy are almost the same as the nonmagnetic calculation. We found that Fe, Co and Ni adatom adsorption has high adsorption energy and migration energy without depending on the spin polarization. Adatoms such as Fe, Co or Ni may make good electrode materials. From this study, we can

electrode materials. As a result of a similar calculation concerning transition metal element adsorption such as Fe, Co, Ni, the possibility to make an electrode material was suggested. High adsorption energy, high migration energy and the graphene surface structure are important physical quantities for electrode materials with graphene.

#### 4.2 Epitaxy

For the epitaxial growth, the migration barrier energy for supplied atom plays an important role. Small migration barrier energy is significant for growing large-area graphene. However, in the case of large migration energy, the epitaxially grown layers on graphene have small grain size. Typically, the small migration energy of 0.03 eV for Cu makes the grain of the large size. Using pulsed laser deposition technique, the growth of GaN on graphite has been succeeded recently. The structure of the grown GaN on graphite is calculated using the density functional theory (Ishii-Tatani-Asano-Nakada and Ishii-Tatani-Nakada ) and the obtained structure agrees well with experiments. For the investigation, the adsorption site of nitrogen adatom on graphite is very important and the adsorption is very similar to the adsorption of N on graphene. Thus, the epitaxial growth on graphene or graphite is possible and will be interesting project in near future.

### 5. Conclusion

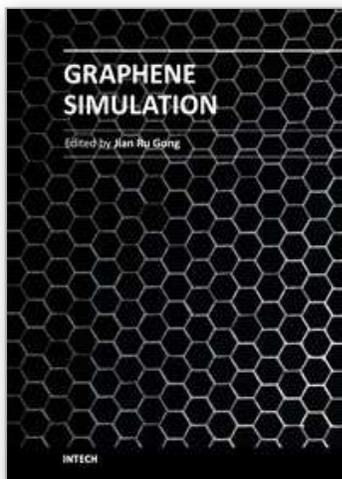
In this research, we calculated the adsorption and migration energy systematically for each adatom adsorbed using the band calculation with the PAW method at three adsorption sites on  $3 \times 3$  graphene. In the case of model metal and transition metal elements, the adatom almost always adsorbed to the H-site and when it was a nonmetallic element we showed that it was mainly adsorbed to the B-site. We showed a tendency to adsorb to the T-site when the number of valence electrons of the adatom is 1, as is the case for H, F, Cl, Br, and I. The stable site for atomic species of transition metals having a very large migration barrier energy (Ti, V, Cr, Mn, Fe, Co, Nb, Mo, Tc, Ru, Ta, W, Re and Os) is H. In transition metal elements, we showed the largest bond energy when the d-orbital is half occupied. The adsorption energy showed a tendency to decrease when the d-orbital occupation exceeded a half. In addition, the adsorption of nonmetallic elements such as C, N, O shows a very large bond energy and adsorption at the B-site. When the d-orbital and s-orbital are occupied, as in Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Cu, Ag and Au, we show a very small adsorption energy. Furthermore, we estimated the minimum limit of the migration energy of the adatom. The tendency for the magnitude of the migration energy is similar to the tendency of the adsorption energy. In the most stable adsorption site, the adatom does not break the structure of graphene. However, in an adsorption site other than the most stable site, we showed that in many cases the adatom breaks the surface structure of graphene. In the growth of a compound semiconductor on graphene, or metal-graphene junctions, we show the importance of the adsorption energy and migration energy. Because Ti and Zr showed good bonding on graphene, we showed that these were useful as electrode materials. Our calculation will be very helpful for experimental groups that are considering the use of atoms and molecules as building blocks, or graphene for making new nano devices, such as nano wires and nano switches.

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