Investigation of Mn adatoms adsorption on graphene using first-principles calculation

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Abstract. The electronic state of the magnetism in a coverage change by multiple Mn atoms and various layout was calculated. When we adsorbed two Mn atoms on graphene, a structure to locate vertical alignment is the most stable. Because difference produces for the large charge transfer between two Mn, large difference of the magnetic moment is created.

1. Introduction
Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities [1]. It can be wrapped up into fullerenes C60, rolled into carbon nanotubes or stacked into graphite. The surface layer of graphite can be considered as the most popular graphene. Nowadays, many researchers are attempting to grow graphene on other surfaces, such as SiC(0001). However, after success in the development of technologies to grow graphene on the surface, the next required technology is to grow the same nano structures on the graphene on the substrate. Thus, graphene will be the focus of attention as a substrate for new nano structure devices using its two-dimensional property. For the functionalization of graphene or the construction of nano structures on graphene, it is necessary to investigate the bonding of materials on graphene. For example, as an important application of the construction of a device on graphene, the growth of GaN thin film on graphite using pulsed laser deposition has been achieved [2, 3, 4, 5, 6]. The structure of the grown GaN on graphite is calculated using the density functional theory [8, 9]. In a theoretical study [7], the adsorption sites and adsorption energies for some atomic species have been reported. However, in general, the mechanism of the growth of three-dimensional materials or nano structures on the two-dimensional material is not yet understood. For the first step, it is necessary to investigate the adsorption of atoms on graphene. In a recent theoretical study [10, 11], we investigate computationally the adsorption energies and migration energies in adsorption sites on graphene sheet for many atomic species, including transition metals, noble metals, nitrogen and oxygen, from atomic number 1 to 83, using the DFT (Density Functional Theory) calculation. We discuss the adsorption and migration energy when an adatom is adsorbed onto graphene. There has been discussion about the adsorption energy in many previous studies [12, 13, 14], if we design a semiconductor device on graphene or a nano device using graphene, the adsorption and the migration energy from an adatom adsorbed onto the graphene are very important. For example, the issue of a metal-graphene junction is an important problem in device design. Therefore, we investigate the stabilities and electronic
structures of adatoms of almost all atomic species to understand the three-dimensional material on graphene, which is itself a typical two-dimensional material. In this study, we perform multiple atomic adsorptions on the graphene. As for the next discussion of the single atom adsorption, it should be discussed by the adsorption of multiple atoms. We chose a Mn atom as an adatom in this research. Because d-orbital is half occupied for the Mn atom, various magnetic order is expected. The electronic state of the magnetism in a coverage change by multiple Mn atom and various layout was calculated.

2. Calculation Method
In this work, we used a first-principles band calculation technique based on density functional theory. We used VASP (The Vienna Ab initio Simulation Package) [15, 16, 17, 18], which is a first-principles calculation code with high precision using the PAW (Projector Augmented Wave) method. We adopted LDA (Local Density Approximation) 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 3×3 structure. The lattice constant of the graphene used the value optimized by calculation. The distance between graphene sheets is about 14.7 Å and the distance between adatoms is about 7.3 Å. The final potential is constructed self-consistently from eigenstates at 24 sampling k-points in the irreducible Brillouin zone (IBZ). To obtain a final band structure, we selected 68 sampling k-points in the IBZ. Two Mn atoms are adsorbed to the 3×3 graphene. For the calculation of adatoms at certain sites, the coordinate normal to the surface is fully relaxed. One atom of the edge of the 3×3 structure of the graphene sheet is fixed during the relaxation of the other carbon atoms of the sheet. The calculation was carried out at many configuration sites. As a result of relaxation calculation, the construction converges in seven pattern shown in Fig.1,2.

3. Result and Discussion
The result of the monoatom adsorption is shown by previous study[10, 11]. When we adsorbed Mn atom on the 3×3 graphene, H-site is more stable and migration energy is 0.14eV. In this study, we adsorbed multiple Mn atom to the 3×3 graphene. We assumed that two Mn atoms have moment of the same direction for DFT calculation. In other words, this would assume ferromagnetism. Fig.1 is local stable structure when two Mn atoms adsorbed it on 3×3 graphene. Fig.1(a) and fig.1(b) are placed in the hexagonal Hollow site (H-site). Fig.1(c) shows that two Mn atom is adsorbed in a six-membered ring. In fig.1(d), two Mn atom is adsorbed each on the direct top of neighboring C atom. As for the configuration of fig.1, two Mn atom is adsorbed each on H-site and the T-site. Fig.1(f) shows that two Mn atom is adsorbed each on H-site and the B-site. Fig.2 shows configuration to locate vertical alignment on H-site. As a result of relaxation calculation, the construction converges in seven pattern shown in Fig.1,2. The configuration that two Mn formed vertical alignment becomes most stable. The energy and the local magnetic moment in the local stable structure were shown in table 1. We show the Δ energy in difference from most stable structure (Fig.2). The d in Table1 shows distance between graphene and the adatom. The m is magnetic moment per Mn atom. The most stability is a fig.2, and configuration most stable next is fig.1(c). Furthermore, the next stable configuration is fig.1(a) and fig.1(d). These stable structure has the special feature that an adjacent distance of two Mn atom is close in. In other words, the dimer structure is stabilized. The fig.1(a) structure of the dimer configuration is slightly unstable to insert C-C atom bond between Mn-Mn dimer. When we located two Mn atom, there are some structures that got different magnetic moment in two Mn atom. In fig.1(e) and fig.1(f) and fig.2 structures, two Mn atoms get different moment. As for the other configuration, two Mn atoms have the same magnetic moment. Firstly we discuss on fig.1(e) and fig.1(f) structure. Atomic magnetic moments of the H-site adsorption side decrease in these structures. It is discussed by Mn monoatom adsorption in the graphene.
A spin magnetic moment of two Mn atom shows large polarization[11]. The magnetic moment of the Mn is made by remaining d-electron after charge transfer occurred from Mn atom to graphene. When the Mn atom adsors in the adsorption site except most stable H-site, the magnetic produces in the Mn atom. In this calculation result, tendency of the magnetic moment in the H,B and T-site adsorption does not have the change either. However, unlike monoatom adsorption, bond distance with the graphene is opened by T-site and the B-site adsorption with H-site adsorption. Therefore, electrons of Mn atom bonding to graphene decrease, and electrons to take magnetic of the Mn atom on increase. The magnetic configuration in fig.2 of the most stable structure is characteristic. When we adsorbed two Mn atoms on graphene, a structure to locate vertical alignment is the most stable. Magnetic moment of the Mn1 of the graphene side is 1.65 $\mu_B$, and the Mn2 of the Mn1 direct top is -0.04 $\mu_B$. Fig.2(c) shows a spin map at this configuration. A spin map is a real space map of magnetization density. As for the yellow in fig.2(c), magnetization density shows a positive region. The negative region is light blue. An interesting magnetic structure is shown in fig.2. Furthermore, we analyze it about charge transfer at this configuration. The charge density analysis checked integral value in the cut-off radius 1.323 $\AA$ in the Mn atom. We performed integral in the cut-off radius 0.863 $\AA$ about the C atom. With the Mn of the graphene side, charge is transferred from Mn1 atom to the graphene side widely then. Furthermore, the Mn atomic charge of the graphene side is transferred to the Mn2 atom of the direct top. In other words, spin magnetic moments decrease because electron to
Figure 2. The most stable structure when two Mn atom adsorbed it.: (a) top view, (b) side view , (c) spin density map

take magnetic on decreases in the Mn1 atom. It is shown that the d-orbital to take magnetic on Mn1 atom decreased remarkably. Furthermore, we calculated the antiferromagnetism and the nonmagnetism status in a structure of fig.2. Because there is five d-orbital, as for the Mn atom, the magnetism with the variety has configuration. As a result, the solution of the ferromagnetic state and the solution of the antiferromagnetic state were degenerated. The antiferromagnetic state of the Mn atom is not kept, because charge is transferred widely in a structure of fig.2. For the calculation that assumed nonmagnetism, fig.2A structure is the most stable. However, a few local stable structure got different result. The structure that trimer of the Mn atoms forms vertical alignment is most stable.

4. Conclusion
We perform multiple atomic adsorptions on the graphene. We found a few local stable structure when two Mn atoms adsorbed to the graphene. When two Mn atoms adsorbed to the graphene top, the Mn atom tends to make a dimer on the graphene. When a Mn atom adsorbed to two sites of H-site and the B-site, magnetic occurred widely in the B-site. Furthermore, magnetic occurred in the T-site when a Mn atom adsorbed to two sites of H-site and the T-site. When we adsorbed two Mn atoms on graphene, a structure to locate vertical alignment is the most stable. In the vertical alignment construction which is the most stable structure, two Mn atomic magnetic moments are different. The magnetic of the Mn was not almost created in the H-site adsorption which was the most stable adsorption site in the monoatom adsorption. However, we could produce magnetic while keeping stable structure because a product displayed two dimers perpendicularly on H site. Because difference produces for the large charge transfer between two Mn, large difference of the magnetic moment is created.
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