Spin-polarized bandgap of graphene induced by alternative chemisorption with MgO (111) substrate

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Abstract

Using First-principle calculations, substrate effect of O-terminated (√3 × √3) MgO (111) on graphene was investigated for spintronics application. Surprisingly, the graphene can be tuned to a spin-polarized semiconductor, which implies that the totally spin-polarized current can be generated and its on/off switching can be also controlled. The origin of the spin-polarized band structure is spin-ordering due to alternative sp2-sp3 covalent bondings induced by the MgO (111) substrate. The results indicate that the tailored pattern of the chemisorption can be highly efficient for introducing totally spin-polarized current to the graphene.

Keywords: magnetic semiconductor, spin-polarized bandgap, first-principles, graphene.

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Spintronics, which is solid state devices based on spin-dependent electron transport, has huge advantages on nonvolatile information processing with low-power-consumption. In the field of spintronics, graphene is expected to produce breakthroughs, due to its long spin lifetime and high mobility.\textsuperscript{1} In particular, the spin coherence length in graphene can reach the micrometer range at room temperature which has very appealing prospects for designing spintronics.\textsuperscript{2} For the realization of graphene-based spintronics, there are still unresolved bottlenecks related to spin filtering. One method to induce a spin-polarized current on the graphene is using the magnetoresistance effect between two magnetic electrodes.\textsuperscript{3-5} Despite the large difference of resistivity between two spin directions in the magnetoresistance device, it is not efficient enough for a totally polarized spin.\textsuperscript{6} A promising alternative method is introducing half-metallicity to the graphene by employing a zigzag nanoribbon structure with an electric field.\textsuperscript{7} However, this strategy requires too strong of an electric field to be realized in real devices. To solve this electric field problem, some new strategies have been proposed, such as edge modification of the nanoribbon,\textsuperscript{8,9} hydrogen patterning,\textsuperscript{10} and B/N doping.\textsuperscript{11} Although these strategies successfully predicted the half-metallicity, there still remains the bottleneck for spin-filtering due to its experimental difficulty of fine control of edge modification, adsorbate patterning and doping in the graphene nanoribbons. In other words, still intensive studies are required to find a realizable way to introduce a totally spin-polarized current to graphene.

Magnetic semiconductors would be the best-suited material for diverse spintronics applications, but not limited to spin-filtering.\textsuperscript{12} Magnetic semiconductors exhibit both ferromagnetism and useful semiconductor properties, which have a huge advantage in controlling both spin-current and charge-current. For this reason, it has a large potential for applications such as spin-polarized light-emitting diodes (spin-LEDs) and spin-polarized field-effect transistors (spin-FETs).\textsuperscript{13} Furthermore, the most important advantage of magnetic semiconductors as potential application is their easy integration into current semiconductor devices. Therefore, there have been intensive efforts to find out suitable magnetic semiconducting materials which have thermal stability and an appropriate bandgap.\textsuperscript{14,15} In this direction, it would be highly desirable to introduce magnetic
semiconducting properties to the graphene, as the half-metallicity is introduced to the graphene.

Tuning the property of graphene by substrate treatment has obvious technological advantages due to its simple process. Recently, Kelber et. al. achieved direct deposition of graphene on a MgO (111) polar surface, and they observed a bandgap opening of the graphene. Furthermore, it was theoretically predicted that periodic chemisorption between graphene and MgO (111) substrate can induce the bandgap of graphene. Those studies imply that the strong interaction between graphene and a MgO (111) substrate results in the modification of the electronic structure of the graphene. Fortunately, the MgO (111) polar surface is prone to be reconstructed into various surface structures because of its surface polarity from its rocksalt structure. In this direction, it is possible that the electronic structure of graphene can be tuned with an oxygen-terminated \((\sqrt{3} \times \sqrt{3})\) MgO (111) phase, one of the experimentally observable reconstruction structures of MgO (111) in a dry condition. In this study, it was investigated that the interface interaction between graphene and \((\sqrt{3} \times \sqrt{3})\) reconstructed MgO (111) results in a magnetic semiconducting property using the Density Functional Theory. Remarkably, the unexpected spin-polarized bandgap was observed, which holds significant technical importance for the realization of spintronics. Furthermore, the spin-polarized bandgap is shown to result from the substrate effect of \((\sqrt{3} \times \sqrt{3})\) the reconstructed MgO (111) surface.

The structure of \((\sqrt{3} \times \sqrt{3})\) MgO (111) is comprised of O-terminated surfaces with 1/3 of the bulk-like O ions missing. The \((\sqrt{3} \times \sqrt{3})\) MgO (111) has 5.19Å of periodicity, which can forms a coincidence lattice with \((2 \times 2)\) unitcell of graphene with 5% strain. The 5% strain of the graphene seems unstable at the interface, but there is sufficient possibility to form an interface with \((\sqrt{3} \times \sqrt{3})\) Mgo (111). In the case of graphene on 6H-SiC, even though it has an 8% lattice mismatch at the interface, the interface structure can stably exist. This is due to the dense chemisorption between graphene and 6H-SiC which overcompensates for the elastic stress at the interface. Even if the elastic stress becomes more dominant and induces corrugation under certain conditions, the chemisorbed interface structure still remains, and significantly contributes to the entire electronic structure of the graphene. Similarly, the graphene on \((\sqrt{3} \times \sqrt{3})\) MgO (111) can
stably exist if the contribution of the interface interaction is more dominant than the elastic strain.

Figure 1a shows the interface structure of graphene on \((\sqrt{3} \times \sqrt{3})\) MgO (111). When the graphene was adsorbed on the \((\sqrt{3} \times \sqrt{3})\) MgO (111) surface, half of the surface oxygen ions were occupied. A carbon atom on top of the occupied surface oxygen moved down to 0.4 Å and a charge transfer occurs, as shown in Figure 1b. 0.21\(e\) of the charge was transferred to the surface oxygen ions which indicate that the chemisorption is formed at the interface. It is expected that the chemisorption would contribute largely to releasing the strain energy of the graphene on the MgO (111). When the 5% strain is introduced to the pristine graphene, the elastic energy amounts to 1.32 eV per coincidence unit cell, which is within typical energetic region of the chemisorption. To determine the stability, the interface energy was calculated. The interface energy was defined by the energy difference between the graphene/MgO(111) and the sum of pristine graphene and the separated MgO (111) substrate. The obtained interface energy was -0.3 eV per coincidence unit cell, which indicates that the interface structure is more stable. However, it should be noted that the obtained interface energy includes the DFT-D2 term, which underestimates the vdW energy of ionized oxygens. This indicates that the strain energy of graphene can be sufficiently released by the chemisorption at the interface and the graphene can be stably placed on \((\sqrt{3} \times \sqrt{3})\) MgO (111). To ensure the stability of the interface, non vdW DFT calculations were also performed as a comparison. The interface energy which did not consider the vdW energy, was -0.01 eV per coincidence unit cell. With a small vdW interaction, the graphene can stably exist on the lattice mismatched MgO (111) substrate.

When the interface was introduced to the graphene, surprisingly, an unexpected magnetic ordering of graphene was observed. The graphene, which was originally a non-magnetic material, became ferrimagnetic on the substrate as shown in Figure 2. In order to ensure the magnetic ground state of the graphene on MgO (111), ferromagnetic, antiferromagnetic configurations and non-magnetic states were also considered by using a \((2 \times 2)\) supercell. In the \((2 \times 2)\) supercell, the geometry of the lattice was identical to the coincidence unit cell and only the ferrimagnetic state was observed. The observed ferrimagnetism was induced by the ordering of the magnetic moment.
of each sublattice of graphene. One sublattice, which occupies the surface oxygen showed -0.06 $\mu_B$ and the other sublattice showed 0.17 $\mu_B$. This magnetic ordering implies that the band structure of the graphene on the MgO (111) surface is spin-polarized.

For a more investigation of the electronic structure of the graphene on the $(\sqrt{3} \times \sqrt{3})$ MgO (111), the spin-resolved band structure was calculated. Remarkably, the magnetic semiconducting property was observed due to the spin-polarized bandgap as shown in Figure 3. In the majority-spin channel, it possessed 2 eV of a very large bandgap, which showed insulating properties. On the other hand, in the minority-spin channel, it showed 0.3 eV of semiconducting bandgap. Such a spin-polarized band structure implies significant technical importance in the generation of spin-polarized current and its on/off switching. Because of the bandgap in the minority-spin channel, the charge transport of the graphene can be controlled by an external electric field and the current flow should be fully spin-polarized. Furthermore, the spin-polarized band structure is obtained without transition metals or external stimuli, so it has a technical advantages in the fabrication processes.\textsuperscript{15,24}

To further understand the physical origin of the substrate-induced ferrimagnetism, the electronic structure of the substrate, the isolated $(\sqrt{3} \times \sqrt{3})$ MgO (111), was investigated. As shown in Figure 4, MgO (111) showed two different spin-states, the non-magnetic state (NM) and the ferromagnetic state (FM). In both states, they showed conductivity. The conductivity of the substrate is contributed by surface oxygen which lost its coordination at the surface. In other words, a hole is injected to the surface oxygen, because fewer electrons are transferred from the cation. It is reported that the injected hole stays in the $2p$ orbital and can be spin-polarized depending on the charged state of the surface oxygen.\textsuperscript{23} The atomic charges of the surface oxygen in FM-MgO and NM-MgO were very similar. The valence electrons of the surface oxygen in FM-MgO (111) and NM-MgO were $6.89e$ and $6.93e$, respectively. On the $(\sqrt{3} \times \sqrt{3})$ MgO (111) surface, the injected hole can exist in either spin-polarized state, FM or NM. It is believed that the existence of both spin states is because of the similar atomic charges of the surface oxygen. Between the two spin-states, NM-MgO (111) is slightly more stable than FM-MgO (111) by 0.15 meV per coincidence unit.
cell, according to our calculation.

When the interface junction is formed, the spin-state of the substrate is drastically changed. **Figure 5a** shows that the DOS of the supercell and the projected density of states (PDOS) of the substrate. The PDOS of the substrate is similar to the -1eV shifted DOS of the FM-MgO (111), though new states were formed near the Fermi level. Furthermore, the substrate, which showed a non-magnetic property in the ground state, became ferromagnetic due to the interface effect. The non-magnetic spin-state in the substrate was no longer observed after the interface was formed. It indicates that there was a spin-state transition in the substrate. The magnetic moment of the surface oxygen of the ferrimagnetic interface was 0.16 $\mu_B$, which was less than that of FM-MgO (111). A more detailed change of magnetic moment value of the other atoms is summarized in **Table 1**. It is deduced that the reduced magnetic moment of the substrate at the interface results from the change of the DOS and a charge transfer from the graphene. Due to the charge transfer, bonded surface oxygen gained 0.2$e$ and un-bonded oxygen gained 0.07$e$. It is believed that the interaction with the graphene should play a dominant role in the spin-polarization of the interface.

In addition to the charge transfer, covalent bonding was also found in the graphene/MgO (111) interface. **Figure 5b** shows that the DOS of the carbon atom in the graphene and the surface oxygen are hybridized near the Fermi level. The carbon has an additional covalent bond with the surface oxygen, and the surface oxygen can only occupy one sublattice of the graphene due to its periodicity. It indicates that the graphene periodically has sp3 hybridization state carbon on one sublattice side. The sp3 hybridized carbon atoms can be a scattering point for the graphene and break the translational symmetry of the lattice. The breaking of the translational symmetry results in the creation of localized states at the Fermi level, where additional electrons or holes in injected to the defect. The localized state allows only a spin-polarized state because of the local electron-electron interaction. For this reason, similar magnetism was also observed in vacancy or hydrogen chemisorption in the graphene, depending on the sublattice symmetry. Therefore, the substrate sp3 state of the graphene also shows the spin-polarization.

In the graphene on the MgO (111), the spin-polarization was not localized at the bonded car-
bon, but delocalized to the entire graphene as shown in Figure 6a. The atoms in the sublattice containing sp3 hybridization showed a negative magnetic moment while the atoms in the other sublattice showed a positive magnetic moment. The PDOS of each sublattice of the graphene on MgO (111) are plotted in Figure 6b. In the graphene on MgO (111), the sublattice containing sp3 hybridized carbon does not have much of the DOS near the Fermi-level. On the other hand, the other sublattice, which consists of only sp2 carbon, showed a rich DOS near the Fermi level. It is deduced that the charge transfer at the interface induced the reduced density of state of bonded carbon atoms, resulting in the ferrimagnetism.

The substrate-induced sp2-sp3 alternative structure can induce the spin-polarized bandgap. The effect of the alternative structure can be characterized by the effect of the covalent bond in one sublattice and the effect of the spin-degeneracy breaking between the two sublattices. When the covalent bond is introduced to the graphene, the band of the graphene can shift. It is because of the energy offset between the substrate and the graphene. Furthermore, the covalent bond decouples the π-electron from one sublattice of the graphene and the induced local imbalance between the two sublattices causes the bandgap. When the spin-degeneracy of the two sublattice is broken, it also induces inequivalency in the sublattices for either spin projection. Because of the exchange interaction and the many-body effect, such an inequivalency results in a spin-polarized band near the Fermi level. The electrons whose spin is parallel (antiparallel) to the net magnetic moment has an energetically favored (unfavored) band. Considering similarities between a majority-spin band in range from -3 to -1 eV and a minority-spin band in range from -1 to 1 eV, it is deduced that the spin polarized bandgap was formed by a shifting and splitting of the band. Therefore, it is believed that the origin of the spin-polarized bandgap is substrate-induced sp2-sp3 alternative bonding and related spin-ordering.

In conclusion, spin-polarized semiconducting property of graphene is achieved by using substrate effect with $(\sqrt{3} \times \sqrt{3})$ MgO (111), which induces sp2-sp3 alternative bonding structure to the graphene. The spin-polarized bandgap can function as a spin valve, which opens up a number of avenues for practical applications of graphene to spintronic devices. The findings imply
that substrate engineering can be a highly effective method for the tuning of graphene electronic
structures. The realization of graphene-based spintronics could be achieved by tailor-made sub-
strate engineering with fine control of the surface magnetism and the periodicity for the interface
bonding.

**Calculation Details**

The graphene on MgO (111) was described using symmetric slab models to avoid the effect of the
internal dipole moment which came from the polarity of the MgO (111) surface. The MgO (111)
surface consists of 13 symmetric layers and the three central slab layers which were kept fixed
with the structural parameter of the bulk MgO. Then, two layers of graphene were adsorbed on the
MgO (111) surface, respectively, with a corresponding periodicity of the reconstructed MgO (111)
structure. In the slab model, at least 12Å of vacuum distance was chosen to avoid interference
with the supercell. All DFT calculations on the supercell were performed with the Vienna *ab-
initio* simulation package (VASP) code, implementing the Perdew-Burke-Ernzerhof exchange
correlation function. The projector augmented wave (PAW) method was employed to describe
the interactions of valence electrons with their atomic cores. Throughout, a plane-wave basis set
was employed to describe a valence electron with a kinetic energy cutoff of 450 eV. All interface
structures were fully relaxed until the maximum total Hellmann-Feynmann force was less than 0.02
eV/Å. The van der Waals (vdW) force was described using the semiempirical correction scheme of
Grimme (DFT-D2). Though the DFT-D2 method can underestimate the binding energy of ionic
systems, it has successfully predicted the geometries of graphene-related structures. The
Monkhosrt-Pack (3 × 3 × 1) k-point grid was used for structural optimizations, and a (7 × 7 × 1)
grid was used to obtain electronic band structures in the (2 × 2) coincidence unit cell. Atomic
charges were estimated by integrating charge densities over cells with a Wigner-Seitz radius. The
other calculation details can be seen in the previous study on graphene on the octo-polar MgO
(111) polar surface.
Acknowledgement

This work was supported by a National Research Foundation (NRF) grant funded by the Korean Ministry of Education, Science and Technology (MEST) grant (No. 2010-0023761), the project of Global Ph.D Fellowship conducted by the NRF in 2011 (No. 2011-0007330), and the Basic Science Research Program through the NRF of Korea funded by the MEST (No. 2011-0016945).

References

1. Pesin, D.; MacDonald, A. H. Spintronics and pseudospintronics in graphene and topological insulators. *Nat. Mater.* 2012, 11, 409–416.

2. Tombros, N.; Jozsa, C.; Popinciuc, M.; Jonkman, H.; Van Wees, B. Electronic spin transport and spin precession in single graphene layers at room temperature. *Nature* 2007, 448, 571–574.

3. Avsar, A.; Yang, T.-Y.; Bae, S.; Balakrishnan, J.; Volmer, F.; Jaiswal, M.; Yi, Z.; Ali, S. R.; Güntherodt, G.; Hong, B. H. et al. Toward wafer scale fabrication of graphene based spin valve devices. *Nano Lett.* 2011, 11, 2363–2368.

4. Cobas, E.; Friedman, A. L.; van’t Erve, O. M. J.; Robinson, J. T.; Jonker, B. T. Graphene as a tunnel barrier: graphene-based magnetic tunnel junctions. *Nano Lett.* 2012, 12, 3000–3004.

5. Kim, W. Y.; Kim, K. S. Prediction of very large values of magnetoresistance in a graphene nanoribbon device. *Nat. Nanotechnol.* 2008, 3, 408–412.

6. Maassen, J.; Ji, W.; Guo, H. Graphene Spintronics: The Role of Ferromagnetic Electrodes. *Nano Lett.* 2011, 11, 151–155.

7. Son, Y. W.; Cohen, M. L.; Louie, S. G. Half-metallic graphene nanoribbons. *Nature* 2006, 444, 347–349.
8. Kan, E.; Li, Z.; Yang, J.; Hou, J. G. Half-metallicity in edge-modified zigzag graphene nanoribbons. *J. Am. Chem. Soc.* **2008**, *130*, 4224–4225.

9. Li, Y.; Zhou, Z.; Shen, P.; Chen, Z. Spin Gapless Semiconductor- Metal- Half-Metal Properties in Nitrogen-Doped Zigzag Graphene Nanoribbons. *ACS Nano* **2009**, *3*, 1952–1958.

10. Zhou, J.; Wang, Q.; Sun, Q.; Chen, X. S.; Kawazoe, Y.; Jena, P. Ferromagnetism in semihydrogenated graphene sheet. *Nano Lett.* **2009**, *9*, 3867–3870.

11. Dutta, S.; Manna, A. K.; Pati, S. K. Intrinsic half-metallicity in modified graphene nanoribbons. *Phys. Rev. Lett.* **2009**, *102*, 96601.

12. Felser, C.; Fecher, G. H.; Balke, B. Spintronics: A Challenge for Materials Science and Solid-State Chemistry. *Angew. Chem., Int. Ed.* **2007**, *46*, 668–699.

13. Jonker, B. T.; Erwin, S. C.; Petrou, A.; Petukhov, A. G. Electrical spin injection and transport in semiconductor spintronic devices. *MRS Bull.* **2003**, *28*, 740–748.

14. Wang, X. J.; Buyanova, I. A.; Zhao, F.; Lagarde, D.; Balocchi, A.; Marie, X.; Tu, C. W.; Harmand, J. C.; Chen, W. M. Room-temperature defect-engineered spin filter based on a non-magnetic semiconductor. *Nat. Mater.* **2009**, *8*, 198–202.

15. Yoo, J. W.; Chen, C. Y.; Jang, H. W.; Bark, C. W.; Prigodin, V. N.; Eom, C. B.; Epstein, A. J. Spin injection/detection using an organic-based magnetic semiconductor. *Nat. Mater.* **2010**, *9*, 638–642.

16. Gaddam, S.; Bjelkevig, C.; Ge, S.; Fukutani, K.; Dowben, P. A.; Kelber, J. A. Direct graphene growth on MgO: origin of the band gap. *J. Phys.: Condens. Matter* **2011**, *23*, 072204.

17. Cho, S. B.; Chung, Y. C. Bandgap engineering of graphene by corrugation on lattice-mismatched MgO (111). *J. Mater. Chem. C* **2013**, *1*, 1595–1600.
18. Ciston, J.; Subramanian, A.; Marks, L. D. Water-driven structural evolution of the polar MgO (111) surface: An integrated experimental and theoretical approach. *Phys. Rev. B* **2009**, *79*, 085421.

19. Tasker, P. W. The stability of ionic crystal surfaces. *J. Phys. C* **1979**, *12*, 4977.

20. Gajdardziska-Josifovska, M.; Crozier, P. A.; Cowley, J. M. A (â£|R 3×â£|R 3) R30Â°r reconstruction on annealed (111) surfaces of MgO. *Surf. Sci.* **1991**, *248*, L259–L264.

21. Subramanian, A.; Marks, L. D.; Warschkow, O.; Ellis, D. E. Direct observation of charge transfer at a MgO (111) surface. *Phys. Rev. Lett.* **2004**, *92*, 26101.

22. Mattausch, A.; Pankratov, O. Ab initio study of graphene on SiC. *Phys. Rev. Lett.* **2007**, *99*, 76802.

23. Zhou, S. Y.; Gweon, G. H.; Fedorov, A. V.; First, P. N.; De Heer, W. A.; Lee, D. H.; Guinea, F.; Neto, A. H. C.; Lanzara, A. Substrate-induced bandgap opening in epitaxial graphene. *Nat. Mater.* **2007**, *6*, 770–775.

24. Du, A.; Sanvito, S.; Smith, S. C. First-Principles Prediction of Metal-Free Magnetism and Intrinsic Half-Metallicity in Graphitic Carbon Nitride. *Phys. Rev. Lett.* **2012**, *108*, 197207.

25. Gallego, S.; Beltrán, J.; Cerdá, J.; Muñoz, M. Magnetism and half-metallicity at the O surfaces of ceramic oxides. *J. Phys.: Condens. Matter* **2005**, *17*, L451.

26. Červenka, J.; Katsnelson, M. I.; Flipse, C. F. J. Room-temperature ferromagnetism in graphite driven by two-dimensional networks of point defects. *Nature Physics* **2009**, *5*, 840–844.

27. Vozmediano, M. A. H.; López-Sancho, M. P.; Stauber, T.; Guinea, F. Local defects and ferromagnetism in graphene layers. *Phys. Rev. B* **2005**, *72*, 155121.

28. Yazyev, O. V.; Helm, L. Defect-induced magnetism in graphene. *Phys. Rev. B* **2007**, *75*, 125408.
29. Kumazaki, H.; Hirashima, D. Nonmagnetic-defect-induced magnetism in graphene. *Physica E* 2008, 40, 1703–1705.

30. Wehling, T. O.; Katsnelson, M. I.; Lichtenstein, A. I. Impurities on graphene: Midgap states and migration barriers. *Phys. Rev. B* 2009, 80, 085428.

31. Daghofer, M.; Zheng, N.; Moreo, A. Spin-polarized semiconductor induced by magnetic impurities in graphene. *Phys. Rev. B* 2010, 82, 121405.

32. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, 54, 11169.

33. Perdew, J.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.

34. Blöchl, P. Projector augmented-wave method. *Phys. Rev. B* 1994, 50, 17953.

35. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* 2006, 27, 1787–1799.

36. Heaton, R. J.; Madden, P. A.; Clark, S. J.; Jahn, S. Condensed phase ionic polarizabilities from plane wave density functional theory calculations. *J. Chem. Phys.* 2006, 125, 144104.

37. Reckien, W.; Janetzko, F.; Peintinger, M. F.; Bredow, T. Implementation of empirical dispersion corrections to density functional theory for periodic systems. *J. Comput. Chem.* 2012, 33, 2023.

38. Bucñko, T.; Hafner, J.; Lebegue, S.; Angyán, J. G. Improved Description of the Structure of Molecular and Layered Crystals: Ab Initio DFT Calculations with van der Waals Corrections. *J. Phys. Chem. A* 2010, 114, 11814–11824.

39. Huang, B.; Xu, Q.; Wei, S. H. Theoretical study of corundum as an ideal gate dielectric material for graphene transistors. *Phys. Rev. B* 2011, 84, 155406.
40. Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.
Table 1: The magnetic moment of each atoms in isolated MgO (111) surface and graphene on MgO (111) interface.

|                      | Non-Magnetic substrate | Ferromagnetic substrate | Ferrimagnetic interface |
|----------------------|------------------------|-------------------------|-------------------------|
| Oxygen               | 0                      | 0.4                     | 0.16                    |
| Bonded Carbon        | -                      | -                       | -0.06                   |
| Unbonded Carbon      | -                      | -                       | 0.17                    |
Figure 1: (a) The topview of the graphene on \((\sqrt{3} \times \sqrt{3})\) MgO (111). The cyan, red and blue balls represent C, O, and Mg atoms, respectively. The black parallelogram indicates the coincidence unit cell of the graphene and the substrate. (b) The sideview and charge density difference of the graphene on \((\sqrt{3} \times \sqrt{3})\) MgO (111). Small corrugation occurs due to carbon atom on the oxygen ion, which moved down to 0.4Å. Then, large charge transfer occurred between the interface, which indicates that the adhesion character is chemisorption.
Figure 2: The magnetic moment of the graphene on $(\sqrt{3} \times \sqrt{3})$MgO (111). Ferrimagnetism was observed in the graphene. One sublattice, which has a bond with the surface oxygen, showed a large positive magnetic moment, while the other sublattice showed a small negative magnetic moment.
Figure 3: The spin-resolved band structure of the graphene on \((\sqrt{3} \times \sqrt{3})\) MgO (111). (a) The bands of majority-spin showed an insulating property with 2.0 eV of large bandgap, while (b) the bands of minority-spin have semiconducting 0.3 eV of semiconducting bandgap.
Figure 4: The Density of state of the isolated substrate. The \((\sqrt{3} \times \sqrt{3})\text{MgO (111)}\) showed two spin states, (a) nonmagnetic state (NM-MgO) and (b) ferromagnetic (FM-MgO).
Figure 5: The projected density of state (PDOS) of the substrate, atoms involved in the interface bonding in the graphene/MgO (111). (a) Shows the PDOS of the substrate in the graphene/MgO (111). When the interface is formed, the substrate became ferromagnetic. (b) Shows the PDOS of the C-O bonding at the interface. The DOS of the carbon is hybridized with the oxygen, which indicates that the carbon has an additional covalent bond.
Figure 6: (a) The spatial spin density difference ($\rho_\uparrow - \rho_\downarrow$) of the graphene on $(\sqrt{3} \times \sqrt{3})$ MgO (111). The isovales for the blue and red isosurfaces are 0.01 and -0.01 e/Å$^3$, respectively. The bonded sublattice forms a minority-spin channel, while the surface oxygen and non-bonded sublattice possess a majority-spin channel. (b) Shows the PDOS of the each sublattice of the graphene. Below the Fermi level, the PDOS of the bonded sublattice was remarkably decreased, compared to non-bonded sublattice.