ENHANCEMENT OF GRAPHENE BINDING ENERGY BY Ti 1ML INTERCALATION BETWEEN GRAPHENE AND METAL SURFACES

TOMOAKI KANEKO^{*,†} and HIROSHI IMAMURA^{*,‡,§}

^{*}*Nanoscale Theory Group, NRI, AIST*
 1-1-1 Umezono, Tsukuba, Ibaraki 305-8565, Japan
[§]*h-imamura@aist.go.jp*

Received 31 December 2011

Revised 20 March 2012

We theoretically investigate the effects of intercalation of a thin Ti layer between graphene (Gr) and metal surface (Au, Ag, Al, Pt, and Pd) on structural and electronic properties by using the first-principles total energy calculations. We find that the strongest binding energy is realized when 1 monolayer (ML) of Ti is intercalated between Gr and a metal surface independent of the metal atoms, which is 0.08–0.15 eV larger than that for Gr adsorbed on a Ti(0001) surface. As the number of Ti layers increases, the binding energy monotonically decreases and converges to that for Gr adsorbed onto the Ti surface. We show that the origin of the enhancement of binding energy can be classified into two classes by considering the affinity of Ti for the metal surfaces.

Keywords: Graphene; First-principles calculations; Binding energy

PACS numbers: 71.15.-m, 73.22.Pr, 71.15.Nc, 61.72.up, 73.29.At

1. Introduction

Graphene (Gr) is an atomically thin carbon sheet that has attracted considerable interest for its application to future electronic devices by virtue of its outstanding transport properties due to the Dirac cone dispersion.¹ To utilize Gr as a basic element of future electronic devices, we need to study the physics of the interface between Gr and metal electrodes. A Ti/Au bilayer is widely used as a metal electrode for Gr^{2,3,4,5,6,7} because Gr is tightly adsorbed onto Ti surfaces compared with other metal surfaces. Recently we have investigated the electronic properties of Gr on Ti/Au surfaces using the first-principles calculations.⁸ We reported that the Gr binding energy is 24% increased compared with that of Ti surface when Ti 1ML is intercalated between Gr and an Au surface.⁸ However, in that report we did not

[†]First-Principles Simulation Group, CMSU, NIMS, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, Japan

[‡]Spintronics Research Center, AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8565, Japan

Fig. 1. (color online) Schematic illustration of the model of Gr structure on M surface. This figure is modified from Ref. [8]. Panels (a) and (b) show top views of Gr on fcc (111) and hcp (0001) M surfaces, respectively. Panels (c) and (d) show side views of Gr on fcc (111) and hcp (0001) M surfaces, respectively.

discuss in detail the enhancement of binding energy. The purpose of the present study is to investigate how Ti 1ML intercalation increases the Gr binding energy.

The effect of contacting the M electrode on Gr is a fundamental issue for the Gr-based device application and many authors have investigated this issue theoretically.^{9,10,11} The strength of Gr binding on the M surface has been regarded as an important factor, because strong binding is needed in order to prevent Gr exfoliation from the M surface. According to the extensive studies by Giovannetti, Khomyakov, and their co-workers, Gr is physisorbed onto Au, Ag, Al, Pt, and Cu surfaces, while chemisorbed onto Pd, Ti, Ni and Co surfaces.^{9,10} The Dirac cone is preserved for physisorbed Gr but disturbed for chemisorbed Gr.^{9,10,11} Thin Ti layer intercalation between Gr and M has been introduced in the electrodes that measure electronic transport in order to tighten Gr binding.^{2,3,4,5,6,7,12,13}

In this paper, we theoretically investigate the effects of Ti intercalation between Gr and several M (Au, Ag, Al, Pt, and Pd) surfaces using the first-principles total energy calculations. We show that the Gr binding energy takes the largest value when 1 ML of Ti is intercalated between the Gr and M surfaces independent of the M species. We elucidate how Ti 1ML intercalation increases the Gr binding energy, and we classify the origin of the enhancement of the Gr binding energy into two classes by considering the affinity of Ti for the M surfaces.

2. Computational details

We performed the first-principles calculations based on the density functional theory within the projector-augmented wave¹⁴ with the plane-wave basis set and the local density approximation (LDA)¹⁵ implemented on VASP code.^{16,17} Gr is adsorbed onto a single side of a metallic slab surface consisting of seven layers as shown in Fig. 1, which is modified from Ref. [8]. In Figs. 1 (a) and (c), the structures of Gr absorbed onto M surface with fcc (111) structure are schematically illustrated. This model is used for Gr adsorbed onto Au, Ag, Al, Pt, and Pd surfaces and Ti intercalated surfaces. For Gr absorbed onto the Ti (0001) surface, we used the structure shown

in Figs. 1 (b) and (d). The cell size is measured by Gr lattice constant $a = 2.446$ Å which is optimized value of free standing Gr in the LDA. Then, the lateral size of the 2×2 supercell of Gr matches the $\sqrt{3} \times \sqrt{3}$ structures of the M surfaces commensurately with mismatch $-1.7 \sim 2.2$ % for optimized bulk lattice structure in the LDA. In the cell, we introduced a vacuum region approximately 14 Å thick and used dipole correction¹⁸ to exclude spurious dipole interactions between periodic images. We relaxed the positions of the C atoms and M atoms in the topmost three layers, but in the topmost four layers in the case of Ti 3ML intercalation. The cut-off energy of the plane wave basis set and the total energy difference were chosen to be 400 eV and 10^{-6} eV, respectively. We used $\mathbf{k}$ -point sampling $18 \times 18 \times 1$ for Gr adsorbed onto Au(111), Ag(111), Al(111), Pt(111), Pd(111), and Ti intercalated surfaces, $12 \times 12 \times 1$ for Ti(0001) surfaces, and comparably dense $\mathbf{k}$ -point sampling for corresponding pristine M surfaces.

3. Results and Discussion

Table 1 summarizes the calculated results of the Gr binding energy, $\Delta E^{(\text{Gr})}$, the averaged separation between Gr and the topmost M atoms, d , the work function of Gr adsorbed onto the M surface, $W_{\text{Gr/M}}$, and the work function of the pristine M surface, W_{M} . The binding energy of Gr is defined as

$$\Delta E^{(\text{Gr})} = \frac{4E_{\text{Gr}} + 3E_{\text{M}} - E_{\text{Gr/M}}}{8}, \quad (1)$$

Table 1. Calculated results of the binding energy of Gr per C atom, $\Delta E^{(\text{Gr})}$, the separation of Gr between the topmost M atom, d , the work function with Gr, $W_{\text{Gr/M}}$, and the work function of the pristine M surface, W_{M} .

	$\Delta E^{(\text{Gr})}$ (eV)	d (Å)	$W_{\text{Gr/M}}$ (eV)	W_{M} (eV)
Au(111)	0.034	3.37	4.79	5.63
Ti 1ML/Au	0.470	2.05	3.91	4.67
Ti 2ML/Au	0.355	2.06	3.97	4.72
Ti 3ML/Au	0.379	2.05	3.87	4.76
Ag(111)	0.032	3.33	4.23	4.90
Ti 1ML/Ag	0.459	2.05	3.90	4.64
Ti 2ML/Ag	0.346	2.06	3.98	4.70
Ti 3ML/Ag	0.378	2.05	3.89	4.77
Al(111)	0.028	3.48	4.06	4.20
Ti 1ML/Al	0.473	2.04	3.91	4.87
Ti 2ML/Al	0.359	2.06	3.95	4.85
Ti 3ML/Al	0.372	2.05	3.90	4.76
Pt(111)	0.045	3.26	4.93	6.00
Ti 1ML/Pt	0.527	2.04	4.10	4.60
Ti 2ML/Pt	0.362	2.07	3.89	4.71
Ti 3ML/Pt	0.374	2.05	3.89	4.79
Pd(111)	0.070	2.45	4.19	4.59
Ti 1ML/Pd	0.508	2.05	4.04	4.55
Ti 2ML/Pd	0.361	2.06	3.91	4.70
Ti 3ML/Pd	0.379	2.05	3.89	4.82
Ti(0001)	0.377	2.05	3.87	4.71

Fig. 2. (color online) The band structures of Gr adsorbed onto Ag(111) and Ti intercalated Ag surfaces. In these Figs. the projections to the p_z orbital of the C atoms are indicated by the blue dots, whose radii are proportional to the magnitude of projection.

where E_{Gr} , E_{M} and $E_{\text{Gr/M}}$ are the total energies of freestanding Gr, the pristine M surface and Gr adsorbed onto M surface, respectively. We found that Gr is physisorbed onto Au(111), Ag(111), Al(111), and Pt(111) surfaces, but chemisorbed onto Pd(111), Ti(0001), and Ti/M surfaces.^{9,10,11} For all M surfaces, as shown in Table 1, the Gr binding energy takes its maximum value when Ti 1ML is intercalated between Gr and M surfaces.⁸ As the thickness of the Ti layer increases, the Gr binding energy monotonically decreases and rapidly converges to that of the Ti surface. d , $W_{\text{Gr/M}}$ and W_{M} also rapidly saturate to that of the Ti surface. Due to the larger resistivity of Ti than other M, it is desirable that an intercalated Ti layer be as thin as possible. Therefore, a Ti 1 ML intercalated surfaces is a good candidate for a practical M electrode for Gr devices.

Figure 2 shows the band structures of Gr adsorbed onto Ag and Ti intercalated Ag surfaces. The band structures of Gr adsorbed onto Ti (0001) and Gr in the doubled unit cell, respectively, are shown in Figs. 2 (e) and (f) as the references. The corresponding Brillouin zone is presented in the inset of Fig. 2 (f). In these Figs. the projections to the p_z orbital of the C atoms are indicated by the blue dots, whose radii are proportional to the magnitude of projection. For Gr on adsorbed onto Ag(111) surface, the Dirac cone survived and the Dirac point is shifted to -0.382 eV due to electron doping from the Ag surface to Gr. However, the Dirac cone disappears by the Ti 1ML intercalation between Gr and Ag surface because the p_z orbital of the C atoms strongly hybridize with d orbital of the Ti atoms. For other M surfaces, the Dirac cone also disappears even by Ti 1ML intercalation.⁸

Table 2. Calculated binding energy of Ti 1ML, $\Delta E^{(\text{Ti1ML})}$, and Gr/Ti 1ML, $\Delta E^{(\text{Gr/Ti1ML})}$, enhancement of Gr binding energy, $\Delta E_{\text{M}}^{(\text{Gr})} - \Delta E_{\text{Ti}}^{(\text{Gr})}$, and binding energy of Ti adatom, $\Delta E^{(\text{Ti})}$.

M	$\Delta E^{(\text{Gr/Ti1ML})}$ (eV)	$\Delta E^{(\text{Ti1ML})}$ (eV)	$\Delta E_{\text{M}}^{(\text{Gr})} - \Delta E_{\text{Ti}}^{(\text{Gr})}$ (eV)	$\Delta E^{(\text{Ti})}$ (eV)
Au(111)	4.61	1.89	0.09	4.42
Ag(111)	4.22	1.53	0.08	3.39
Al(111)	4.56	1.83	0.10	3.87
Pt(111)	5.75	2.87	0.15	7.86
Pd(111)	5.43	2.61	0.13	7.58
Ti(0001)	4.72	2.25	—	5.94

Finally we consider how Ti 1ML intercalation increases the Gr binding energy. The enhancement of Gr binding energy by Ti 1ML intercalation from that of the Ti surfaces can be written as follows:

$$\Delta E_{\text{Ti1ML/M}}^{(\text{Gr})} - \Delta E_{\text{Ti}}^{(\text{Gr})} = \frac{3}{8} (\Delta E_{\text{M}}^{(\text{Gr/Ti1ML})} - \Delta E_{\text{Ti}}^{(\text{Gr/Ti1ML})} - \Delta E_{\text{M}}^{(\text{Ti1ML})} + \Delta E_{\text{Ti}}^{(\text{Ti1ML})}), \quad (2)$$

where $\Delta E^{(\text{Ti1ML})}$ and $\Delta E^{(\text{Gr/Ti1ML})}$ are the binding energies of Ti 1ML and Gr/Ti 1ML per Ti atom, respectively. The calculated $\Delta E^{(\text{Ti1ML})}$ and $\Delta E^{(\text{Gr/Ti1ML})}$ are summarized in Table 3.

For the Au(111), Ag(111) and Al(111) surfaces, the binding energies of Gr/Ti 1ML and Ti 1ML are smaller than those for the Ti(0001) surfaces. The differences in the binding energies of Ti 1ML on these M surfaces between Ti(0001) are much larger than those of Gr/Ti 1ML. Therefore, the enhancement of the Gr binding energy is caused by the weak binding of Ti 1ML to these M surfaces. On the other hand, both Gr/Ti 1ML and Ti 1ML are tightly adsorbed onto Pt(111) and Pd(111) surfaces compared with those onto Ti(0001) surfaces. In these cases, the tight adsorption of Gr/Ti 1ML onto the M surfaces enhances the Gr binding energy by Ti 1ML intercalation. We found that the enhancement of the Gr binding energy can be classified into two classes.

This classification is based on the affinity of the Ti atom for M surfaces. The last row of Table 2 presents the binding energy of Ti adatom on the $\sqrt{3} \times \sqrt{3}$ structure M surface per Ti atom $\Delta E^{(\text{Ti})}$. We found that adsorption of Ti atom on Au(111), Ag(111), and Al(111) surfaces are much weaker than that on Ti surface, while those on Pd(111) and Pt(111) surfaces are much stronger than that on Ti surface. Since these behaviors agree well with those for the binding of Ti 1ML, these results indicate that the different affinities of Ti and several M surfaces activate different mechanisms of the enhancement of Gr binding energies.

4. Summary

We investigated the effects of the intercalation of a thin Ti layer between graphene and several metal surfaces (Au, Ag, Al, Pt, and Pd) on structural and electronic properties using the first-principles total energy calculations. We found that Ti 1ML intercalation enhances the graphene binding energy by 0.08-0.15 eV from that for the

Ti surface. The graphene binding energy monotonically decreases as the thickness of the intercalated Ti layer increases. The enhancement of the binding energy can be divided into two classes. For Au, Ag, and Al surfaces, the enhancement of graphene binding energy is caused by the weaker binding of Ti 1ML on M surfaces than on Ti surfaces. For Pt and Pd surfaces, on the other hand, the enhancement of graphene binding energy is caused by the stronger binding of the bilayer of graphene and Ti 1ML than the Ti surface. The origin of the difference is the different affinities of Ti and different metal surfaces.

Acknowledgments

The authors acknowledge T. Nakano, Y. Shimoi, K. Harigaya, and H. Arai for their valuable discussions. This research was supported by the International Joint Work Program of Daeduck Innopolis under the Ministry of Knowledge Economy (MKE) of the Korean Government.

References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, **306**, 666 (2004).
2. E. J. H. Lee, K. Balasubramanian, R. T. Weitz, M. Burghard and K. Kern, *Nature Nanotechnology*, **8**, 486 (2008).
3. B. Huard, N. Stander, J. A. Sulpizio and D. Goldhaber-Gordon, *Phys. Rev. B*, **78**, 121402(R) (2008).
4. K. Nagashio, T. Nishimura, K. Kita and A. Toriumi, *Appl. Phys. Lett.* **97**, 143514 (2010).
5. S. Russo and M. F. Craciun, M. Yamamoto, A. F. Morpurgo and S. Tarucha, *Physica E*, **42**, 677 (2009).
6. J. A. Robinson, M. LaBella, M. Zhu, M. Hollander, R. Kasurda, Z. Hughes, K. Trumbull, R. Cavaleiro and D. Snyder, *Appl. Phys. Lett.* **98**, 053103 (2011).
7. P. Blake, R. Yang, S. V. Morozov, L. A. Ponomarenko, A. A. Zhukov, R. R. Nair, I. V. Grigorieva, K. S. Novoselov, A. K. Geim, *Solid State Commun.*, **149**, 1068 (2009).
8. T. Kaneko and H. Imamura, *Appl. Phys. Lett.*, **98**, 261905 (2011).
9. G. Giovannetti, P. A. Khomyakov, G. Brocks, V. M. Karpan, J. van den Brink and P. J. Kelly, *Phys. Rev. Lett.*, **101**, 026803 (2008).
10. P. A. Khomyakov, G. Giovannetti, P. C. Rusu, G. Brocks, J. van den Brink and P. J. Kelly, *Phys. Rev. B*, **79**, 195425 (2008).
11. C. Gong, G. Lee, B. Shan, E. M. Vogel, R. M. Wallance and K. Cho, *J. Appl. Phys.*, **108**, 123711 (2010).
12. H. B. Heersche, P. Jarillo-Herrero, J. B. Oostinga, L. M. K. Vandersypen and A. F. Morpurgo, *Nature*, **446**, 56 (2007).
13. T. Mueller, F. Xia, M. Freitag, J. Tsang, and Ph. Avouris, *Phys. Rev. B*, **79**, 245430 (2009).
14. P. Blöchl, *Phys. Rev. B*, **50**, 17953 (1994).
15. J. P. Perdew and A. Zunger, *Phys. Rev. B*, **23**, 5048 (1981).
16. G. Kresse and J. Furthmüller, *Phys. Rev. B*, **54**, 11169 (1996).
17. G. Kresse and J. Furthmüller, *Comp. Mat. Sci.*, **6**, 15 (1996).
18. J. Neugebauer and M. Scheffler, *Phys. Rev. B*, **46**, 16067 (1992).