Potential-Energy Surface of Graphene on Transition-Metal Surfaces

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Abstract

The nature of graphene/metal interface is of great interest for understanding graphene growth by chemical vapor deposition. We have calculated the potential-energy surface (PES) of graphene on catalyst transition-metal surfaces. We found that the adsorption state of graphene varies from chemisorption at the minimum of PES to physisorption at the maximum of PES. The minima of PES highly depend on the type of metal, whereas the maxima of PES are nearly independent. The order of PES roughness is Cu < Ni < Co. The level of metal d-band is a key factor for PES roughness and the adsorption state of graphene.

1. Introduction

Chemical vapor deposition (CVD) growth of graphene films has been widely studied using catalyst transition-metals due to its scalability [1-3]. However, structural disorder caused by the formation of graphene domains significantly affects the characteristics of graphene films [4, 5]. The boundaries of graphene domains are supposed to be formed by the coalescence of misaligned graphene islands. The migration of graphene islands at the initial stage of CVD growth should be influenced by the distribution of the binding energies, i.e., the potential-energy surface (PES).

In this study, we have investigated systematically the PES's of graphene on transition-metal surfaces. To obtain the PES's we calculated the binding energies of different configurations of graphene on the metals by using a density functional theoretical method. We compare the PES's for different metals and examine the substrate dependence of PES profile.

2. Calculation method

Our calculations were carried out using STATE [6]. Because van der Waals (vdW) forces can remarkably contribute to the interactions between graphene and metals [7, 8], we used the second-version of van der Waals density functional (vdW-DF2) [9] with the exchange functional of Cooper (C09) [10].

Co(0001), Ni(111), and Cu(111) were employed as the catalyst transition-metal surfaces. The metal surfaces were represented using the slab model where one slab consists of 6 atomic-layers. A graphene layer was adsorbed on the clean metal surface, and fitted to the metal (1×1) surface unit cell (Fig. 1) because the lattice of the metals matches that of graphene.

Figure 1 shows the configuration of graphene on metal

surface. The parameters X and Y represent the position of the graphene as distance of a C atom from an on-top (top) site along the x- and y-axis's, respectively. The high symmetry points of top, hcp-hollow (hcp), and fcc-hollow (fcc) sites are aligned along the line of X = 0 at equal interval of D. The parameter Z represents the height of the graphene from the first layer of the metal surface.



Fig. 1: (a) Top and (b) side views of the atomic structure of a graphene/metal system.

3. Results and discussion

We calculated the binding energies per C atom (BE) as BE(X, Y, Z) = $E^{\text{Gr/M}}(X, Y, Z) - E^{\text{Gr}} - E^{\text{M}}$ (1),

where $E^{\text{Gr/M}}(X, Y, Z)$, E^{Gr} , and E^{M} are the energies of the adsorbed system, the isolated graphene, and the clean metal surface, respectively. The system with fixed *X* and *Y* has an equilibrium at $Z = Z_{\text{eq}}$ where BE(*X*, *Y*, *Z*) has the minimum value of BE_{eq}(*X*, *Y*) = BE(*X*, *Y*, *Z*_{eq}). PES for the graphene/metal systems is defined as the distribution of BE_{eq}(*X*, *Y*) (Fig. 2). The BE_{eq} value varies with the position of graphene. The maximum and minimum sites of PES lie on the line of X = 0.



Fig. 2: Binding energies at the equilibrium (BE_{eq}) as functions of *X* and *Y* $(BE_{eq}(X,Y))$, or PES, for the graphene/Ni system.

We compared the distributions of the BE_{eq} along the X = 0 line (BE_{eq}(Y)) for Co, Ni, and Cu (Fig. 3). Here, "top-hcp" denotes the adsorption site of the graphene at Y = 0 on the metal surfaces where the C atoms in the unit cell are placed at the top and hcp sites. As seen in Fig. 3, the PES for Cu is nearly flat while those for Ni and Co are rough. BE_{eq}(Y) on the three metals has the maximum (BE^{max}_{eq}) at hcp-fcc site and the minimum (BE^{min}_{eq}) at fcc-top site. Note that the BE^{max}_{eq} values are almost the same on different metal surfaces. In contrast, the BE^{min}_{eq} values greatly depend on the type of underlying metals, and the order of the absolute BE^{min}_{eq} value is Cu < Ni < Co.





We examined the adsorption state of graphene with the metals at the maximum (BE_{eq}^{max}) and minimum (BE_{eq}^{min}) of PES. We found that vdW interaction is the major component of the calculated $BE_{\scriptscriptstyle eq}^{\scriptscriptstyle max}\;$ value. The graphene at the maximum of PES, or hcp-fcc site, is physisorbed. On the other hand, the substrate dependence of $BE_{\mbox{\tiny eq}}^{\mbox{\tiny min}}$ suggests that the graphene at the minimum of PES, or fcc-top site, is chemically bound to the metals. To visualize the chemical bond, we calculated the electron density difference of the adsorbed systems (Fig. 4). Here, the electron density difference denotes the subtraction of the electron densities of the isolated graphene and the clean metal from that of the adsorbed system. Graphene sp³ electrons increase, especially in between graphene and the metals, which induces the chemical bond. The order of the degree of increased sp³ electrons is Cu < Ni < Co, which corresponds with that of the absolute BE_{eq}^{min} values.

Our examination shows that the adsorption state of graphene with the metals varies from physisorption at hcp-fcc site to chemisorption at fcc-top site. The order of PES roughness is Cu < Ni < Co and reflect the difference in the strength of chemical bond at the most stable site. Our further investigation reveals that the interaction between graphene and metal d-band is largely responsible for PES roughness. The large roughness of the PES may contribute to the stabilization of graphene islands with respect to translation or rotation. The substrate dependence of PES

profile and the level of metal d-band can be a clue to elucidate the process of CVD growth at the initial stage.



Fig. 4: Isosurfaces of the electron density difference of the graphene adsorbed at the most stable site on (a) Co, (b) Ni, and (c) Cu. Red (blue) regions denote electrons increase (decrease) compared to the isolated systems. The isovalue is ± 0.03 electron/nm³.

4. Conclusions

We have studied the PES of graphene on transition-metal surfaces using density-functional theoretical calculations. We found that the adsorption state of graphene with the metals varies with the position of graphene. The graphene at the maximum of PES is physisorbed, and the binding energy of the graphene is almost insensitive to the type of metals. On the other hand, the graphene at the minimum of PES is chemisorbed, and its binding energy is highly sensitive to the underlying metals. The PES for Cu is nearly flat whereas those for Ni and Co are rough. The degree of PES roughness is largely affected by the level of metal d-band. The trend of PES roughness found in this work can contribute to the future research of CVD graphene growth.

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