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Epitaxial graphene monolayer and bilayers on Ru(0001): *Ab initio* calculations

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We studied very large graphene/Ru systems by *ab initio* calculations. It is shown that the graphene monolayer on Ru is nearly flat rather than strongly corrugated. The large corrugation is found to be unfavorable and disagrees with the observed bias dependence of scanning tunnel microscope images. The C-Ru bonds are metallic instead of covalent. A new moiré structure arises between graphene bilayers and the generally supposed Bernal stacking is broken. The second layer has higher density of C atoms and is slightly corrugated. While the electronic states of the first graphene layer are shifted down by about 1 eV, the electronic structure of the second one resembles that of the free graphene, in good agreement with the experiments.

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I. INTRODUCTION

Since the discovery of graphene,[1] a vast number of studies have been devoted to this one-atom-thick planar material due to its unique and fascinating properties, such as extreme high electron mobility,[2,3] room-temperature quantum-Hall effect[2,4] and 100% spin-polarized carriers under electric field.[5] Recently, there has been a great breakthrough in producing graphene layer on Ru(0001) with unprecedented sizes over 100 μm and even millimeters in length, well exceeding the sizes achieved previously.[6–8] A large piece of second graphene epilayer has been grown above the first one and begins to function as free graphene.[6,9,10] These progresses have opened up a different avenue to the graphene-based nanoelectronics.

In spite of the great success in producing graphene layers on Ru, their fundamental properties remain unclear. Especially, the study of the newly synthesized second graphene layer is just beginning and there are many are to be explored. It is imperative to study their morphology, bonding character, and electronic structure, the knowledge of which is a prerequisite for applications. The morphology of the graphene monolayer on Ru determines the properties of itself as well as the layers above and therefore is of crucial importance. Strong atomic corrugations seem to be suggested by surface x-ray diffraction (SXRD) and scanning tunnel microscope (STM) measurements,[11] the inhomogeneous C-Ru bonding[12,13] and some previous calculations.[14,15] However, the He atom scattering[16,17] indicates only small atomic ripples. The angle-resolved photoemission spectroscopy (ARPES) experiments[9,12] agree very well with the calculated band structure of the commensurate (1×1) *flat* graphene/Ru. These disagreements are to be solved before studying other properties of graphene/Ru. The C-Ru bonding were generally supposed to be covalent,[6,14,18] which usually leads to a semiconducting interface. Since graphene is a semimetal, it can be questioned whether it is covalently or metallically bonded to Ru. In contrast to the complex moiré structures identified between graphene monolayer and Ru,[11,16,18] the second graphene layer is usually thought to be a flat layer over the first one with Bernal stacking.[6,9] However, a much more complex structure might occur between the graphene bilayers due to the strong Ru-graphene interaction and the weak graphene-graphene interaction. To address these important issues, we studied very large systems of graphene monolayer and bilayers on Ru(0001) by density-functional calculations. It is revealed that the *periodic* strongly corrugated graphene/Ru[14,15] is unfavorable and does not agree with the observed bias dependence of the STM images.[16,18] The graphene/Ru system prefers to be quasiperiodic, which is found to be nearly *flat* and stretched, and is much more strongly bonded to Ru and thus much more favorable. The flat graphene/Ru agrees with the STM observations very well. The C-Ru bonds are identified as metallic. There is considerable mismatch between the graphene bilayers, resulting in a new moiré structure between them. The C atoms in the second layer are more densely packed than in the first one. The second layer also has small corrugations. Its electronic structure resembles that of the free graphene.

II. COMPUTATIONAL METHODS

The calculations are performed by using VASP.[19] The electron-core interaction is described by projector augmented wave potentials[20,21] and the local density approximation is used in the form of Ceperley-Alder.[22] The cutoff for plane-wave expansion is 300 eV. The calculated lattice parameters of Ru are $a=2.68$ Å and $c=4.233$ Å, and the C-C bond length in free graphene is 1.42 Å. We have studied several very large graphene/Ru systems, which will be detailed below. The vacuum layer between the slabs is about 10 Å. Only the Γ point of Brillouin zone is used due to the large lateral size of the systems. The bottom Ru layer is fixed and other atoms are relaxed until the forces are smaller than 0.02 eV/Å. In the following, we use graphene$(m\times m)$ and Ru$(n\times n)$ to denote *strictly* periodic structures in which there are m graphene primitive units and n Ru(0001) primitive units, respectively. Graphene$(m\times m)$/Ru$(n\times n)$ stands for a strictly periodic structure in which m graphene primitive units are matched to n Ru(0001) primitive units.

III. RESULTS AND DISCUSSION

We first address the graphene monolayer on Ru(0001). Due to the mismatch between their primitive cells, the result-

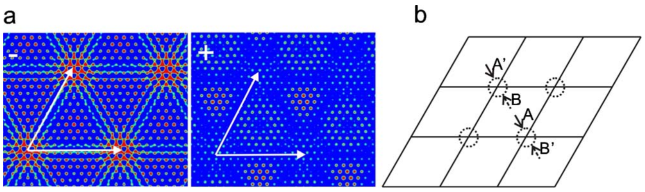

FIG. 1. (Color online) (a) The simulated STM image of the rigid model of flat graphene(12×12)/Ru(11×11) with a fixed C-Ru separation of 2.1 Å. Red and blue denote high and low electron density, respectively. The '−' and '+' signs indicate the polarity of the bias. (b) The schematic illustration of the corrugation induced by the periodic constraint. The dotted circles denote the high regions of the graphene monolayer on Ru(0001). A′ and B′ in the neighboring cells are the images of A and B. The arrows indicate the direction of the atoms tending to move.

ing moiré structure is very complex, which can be *quasiperiodic* or coincidentally *periodic*.[18,23] Graphene(12×12) and Ru(11×11) almost fit with each other. Currently, the moiré cell is usually approximated by periodic graphene(12×12)/Ru(11×11) because they have nearly the same size.[14–16,18] We calculated this periodic system by using a slab of one graphene(12×12) layer and three Ru(11×11) layers (288 C atoms and 363 Ru atoms, 651 atoms in total) and the results are very similar to the previous ones.[14,15] The graphene has a large corrugation of 1.76 Å (the lowest point is 2.1 Å above Ru), which is very unfavorable, costing an extra energy of 3.4 eV per graphene(12×12) cell.[14] The hill-like features in STM images seem to indicate large geometric corrugations in graphene but they can also arise from electronic modulation.[18,23] The strong bias dependence of STM images, however, suggests strong electronic effect instead of geometric effect.[16,18] We calculated the STM images of the strongly corrugated graphene(12×12)/Ru(11×11), varying the bias from −2 to +2 V with an interval of 0.5 V. However, the calculated STM images under all biases are similar to Fig. 1d in Ref. 14 and do not show the bias dependence. This is because that the corrugation is so large (1.76 Å) that the geometric effect is far more dominant than the electronic effect. Therefore, the high regions are invariably much brighter than the low regions under all biases, disagreeing with the experiments.[16,18] As will be shown below, the true morphology of graphene/Ru is quasiperiodic and nearly flat, slightly deviating from the flat graphene(12×12)/Ru(11×11). Therefore, the *flat* rather than strongly corrugated graphene(12×12)/Ru(11×11) is a better approximation to the quasiperiodic moiré structure if morphology is of the only concern. We simulated STM images of the rigid model of *flat* graphene(12×12)/Ru(11×11) with a fixed C-Ru separation of 2.1 Å [Fig. 1(a)]. The experimental STM images are well reproduced and the brightest regions become very dark when the bias polarity alters from negative to positive, suggesting that a flatter graphene/Ru agrees better with the experiments.[16,18] All these require a reconsideration of the model of strongly corrugated graphene(12×12)/Ru(11×11). Figure 1(b) illustrates how large corrugations can be induced by the enforced strict periodicity in calculations. The calculations find that the C-C bonds in the low and bonding regions are stretched from 1.43 to 1.45 Å. Therefore, the C atoms in the other regions of the periodic cell are considerably compressed together and pushed up. The C atoms near the highest regions are about 3.86 Å above the substrate and not bonded to Ru. Within the periodic model, the highest C atoms can be assumed to locate at the four corners of the surface unit cell of graphene/Ru [see Fig. 1(b)]. They tend to stretch outside of the unit cell. However, this is impossible. When atoms in regions A and B move outward, their periodic images in regions A′ and B′ just move against them. In reality, the C atoms are relaxed to lower the energy and release the stress rather than follow a given periodicity. Supposing that the deviations from the strict periodicity are allowed, then the C atoms around the corners can move more freely, significantly reducing their stress and height and increasing the number of C atoms bonded to Ru atoms (see below). Therefore, it is more realistic to go beyond the strict periodic model and adopt the quasiperiodic model to allow the small deviations in calculation. Actually, the experiments cannot discriminate between the *coincidental strict* periodicity and the *quasiperiodicity*.[18,23]

To take into consideration of the small deviations in the quasiperiodic graphene/Ru, we calculated very large graphene cluster within the surface cell of the two-layer Ru(0001)-(15×15) slab ($C_{390}H_{54}Ru_{450}$, 894 atoms in total) [Fig. 2(a)].[24] The lateral size of the supercell Ru(0001)-(15×15) is considerably larger than that of the graphene cluster and hence is enough to decouple the images of graphene cluster in the periodic supercells. The cluster has much more C atoms than graphene(12×12) (288 C atoms) and covers all kinds of C adsorption sites in graphene(12×12)/Ru(11×11). Therefore, it can address the complex graphene-Ru interaction in all regions of graphene/Ru. For comparison, we calculated three systems, labeled as G_1, G_2, and G_3. They have different initial structures and their final structures and energies are also different. To be clear, we label the initial structure before relaxation and the final structure after relaxation of G_n $(n=1,2,3)$ by G_n^i and G_n^f, respectively. The graphene in G_n^i $(n=1,2,3)$ is 2.1 Å above Ru(0001). G_2^i simulates the initial structure of the periodic graphene(12×12)/Ru(11×11) that was adopted in the previous calculations[14,15] so that they have the same graphene-Ru relative positions. Since we have already found that graphene is appreciably stretched in the region where C atoms are low and strongly bonded to Ru (see above), we stretched graphene uniformly to a similar extent in G_1^i in order to obtain a strongly coupled graphene-Ru structure. It turns out that G_1^f is almost flat and stretched after relaxation. A large part of G_2^f is also stretched and almost flat while a small part of it has a corrugation of 1.4 Å. G_1^f is 7.1 eV lower in energy than G_2^f, showing that a stretched and nearly flat graphene/Ru is much more energetically favorable. This is because that there are much more C atoms strongly bonded to Ru in G_1^f than in G_2^f. To confirm this idea, the C atoms in the raised part of the G_2^f are pushed down so that there are more C atoms strongly interacting with Ru atoms. In this way we obtain the initial structure of G_3, i.e., G_3^i. After relaxation, G_3^f is almost flat and is 2.8 eV lower in energy than G_2^f (i.e., G_3^i). Their number of the C atoms bonded to the top sites of Ru(0001) and their stability follow the sequence $G_1^f > G_3^f > G_2^f$, showing that the larger the number of C atoms bonded

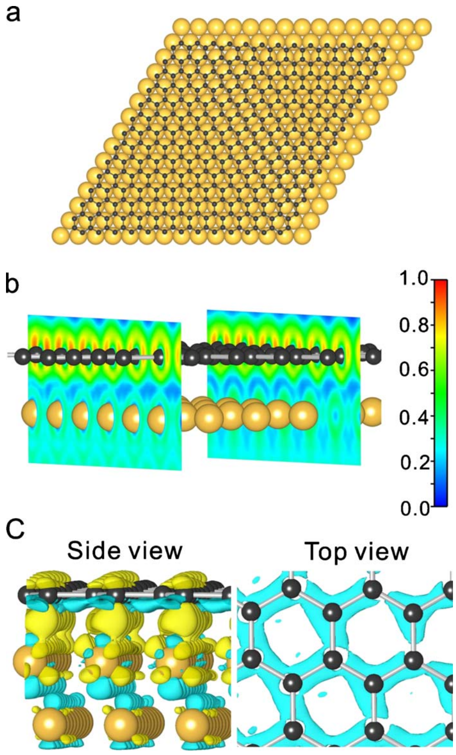

FIG. 2. (Color online) (a) The top view of the nearly flat quasiperiodic graphene on Ru(0001). For clarity, only the C atoms and the first layer of Ru(0001) are shown. The black and orange spheres denote the C and Ru atoms, respectively. (b) ELF in two slices. (c) Charge transfer between the graphene monolayer and Ru(0001). The positive and negative values are shown in yellow and cyan on the isosurfaces ($\rho = \pm 0.008$ electrons/bohr^{-3}), respectively. In the top view, only the negative value is plotted. For clarity, the graphene cluster and Ru(0001) is partially shown in (b) and (c).

to Ru, the more stable the system and hence the large corrugations are very unfavorable. Hereafter, we only discuss the most favorable structure G_1^f. The maximum corrugation of G_1^f is found to be 0.24 Å, in good agreement with the value (0.2 Å) measured by He scattering.[16,17] The average graphene-Ru distance is 2.1 Å and the C-C bond lengths range from 1.43 to 1.49 Å. The largest corrugation of the first Ru layer is 0.15 Å, close to the experimental value of 0.2 Å.[11] The hexagonal symmetry is well-preserved in G_1^f, indicating quasiperiodicity with only small deviations. Experiments observed different C-Ru binding energies[13] and the electrostatic potential energy surface with a corrugation of 0.24 eV,[12] suggesting inhomogeneous C-Ru bonding. In the scenario of strongly corrugated graphene/Ru, it is explained by different graphene heights on Ru.[12,13] In fact, in the nearly flat graphene/Ru, some regions have more (fewer) C atoms close to the top sites of Ru and hence are more strongly (weakly) bonded to Ru, which can produce the inhomogeneous C-Ru bonding, as well. Interestingly, Brugger found that the geometric corrugation obtained by previous calculations[14,15] is too large if compared with their experiment.[12] A corrugation of 1.5 Å is tentatively suggested by fitting the SXRD data to a simple model.[11] However, it uses the large theoretical graphene corrugation[14] as parameter and ignores the important in-plane movements.[11]

Sutter *et al.*[9] found that in the registries where carbon atoms are nearly or right above the Ru atoms, the binding energy is about 0.4–0.45 eV per carbon atom, demonstrating a significant chemical interaction upon interface formation. A strong covalent bonding is generally supposed between C and Ru atoms.[6,14,18] Because graphene is a semimetal and Ru is a metal, the C-Ru bond is more likely to be metallic. We calculated the electron localization function (ELF) (Refs. 25 and 26) of G_1^f, as shown in Fig. 2(b). ELF is very useful and visually informative in describing whether a bond is formed between two atoms and what the character of this bond is (e.g., covalent, ionic, or metallic). The electrons are very localized in the region where ELF is close to unity, while they are as delocalized as free electrons if ELF is around 0.5. In our calculations as shown in Fig. 2(b), there are regions connecting C and Ru atoms in which the ELF is about 0.5, showing that metallic bond is formed. Our calculations show that each C atom in the first graphene layer averagely obtains 0.02 electrons from Ru substrate. To further study the spatial distribution of the charge transfer between the graphene monolayer and Ru(0001), we calculated the charge density of three systems: graphene/Ru(ρ) (i.e., G_1^f), graphene only (ρ_g) and Ru only (ρ_{Ru}). The last two systems are fixed to be the same as their counterparts in the first one (G_1^f). The charge difference ($\rho - \rho_g - \rho_{Ru}$) is shown in Fig. 2(c). Usually, C atoms are expected to obtain electrons from Ru atoms. We find this is only true for C π bonds but not for the C-C σ bonds. It can be seen in the side view of Fig. 2(c) that the charge density is increased in the region right above and below the C atoms, indicating that the π bonds obtain electrons from Ru. In the top view, one can see that the charge density is decreased in the region near the σ bonds, showing that the σ bonds lose rather than obtain electrons, which explains why the C-C bonds are stretched and weakened and why the phonons are softened in graphene/Ru.[27]

Now we study the second graphene epilayer on Ru. Above the first layer of graphene cluster on Ru(15×15), the second graphene cluster is added ($C_{390}H_{54}C_{390}H_{54}Ru_{450}$, altogether 1338 atoms) in Bernal AB stacking, which is generally assumed between the graphene bilayers.[6] As found above, the first layer of graphene cluster is stretched. To keep the Bernal stacking, the second one is equally stretched to be commensurate with the first one in the initial configuration. After relaxation, we find that the first graphene layer almost does not change while the second one contracts with respect to the first one. The second layer is close to free graphene with average C-C bond length of 1.42 Å. Therefore, the first two graphene layers are incommensurate. In Fig. 3, it can be seen that the incommensurance is increasingly apparent from the center to the four corners. Hence a new moiré structure appears between the graphene bilayers. Clearly, there are more carbon atoms in the unstretched second layer than in the stretched first layer per unit area (Fig. 3). In *periodic* model in which the two graphene layers have the same number of C atoms, the new moiré structure cannot be observed. For interlayer π-bond interaction, the Bernal AB stacking is preferred. On the other hand, the in-plane σ-bond interaction tends to keep the C-C bond length of the free graphene. Since σ bonds are much stronger than π bonds, it is very unfavorable to stretch the C-C bonds of the second graphene

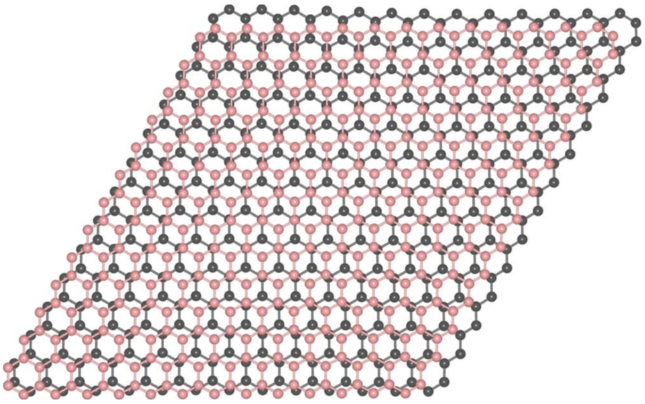

FIG. 3. (Color online) The top view of the graphene bilayer moiré on Ru(0001). For clarity, only the graphene bilayers are shown. The black and salmon spheres denote the C atoms in the first and second graphene layer, respectively.

layer to keep the Bernal AB stacking. The origin of the graphene bilayer moiré structure is due to the strong bonding between the graphene monolayer and Ru(0001), which expands the graphene monolayer, and the weak interaction between the graphene bilayers, which is not enough to expand the second graphene layer. Such moiré structure should occur in most of the graphene epitaxial bilayers, because the first graphene layer usually strongly interacts with the substrate and hence is stretched or compressed. The incommensurance between the graphene bilayers produces a maximum corrugation of 0.14 Å in the second graphene layer. The average spacing between the graphene bilayers is found to be 3.29 Å, in good agreement with the experiments.[6] It is known that AB stacking is more favorable than AA stacking in free-standing graphene bilayers. In the graphene bilayer/Ru system, the mismatch between graphene bilayers leads to AB-like stacking in one part and AA-like stacking in other part (Fig. 3). Therefore the binding between the suspended graphene bilayer in AB stacking is stronger than that between the graphene bilayer on Ru with inhomogeneous stacking. It can be expected that the third and the subsequent graphene layers would be in closer and closer Bernal stacking with the layer below it and is flatter and flatter. We estimate that the mismatch between the second and third layer of graphene above Ru should be very small because the second layer is already quite close to the free-standing graphene.

We have also calculated the partial densities of states (PDOS) of the carbon ring at the center of the first and second graphene cluster layers, which are shown in Fig. 4 together with the PDOS of the free graphene. The PDOS of the first graphene layer is almost the same as that when the second graphene layer has not been added. The PDOS of the first graphene layer at the Fermi level is finite, indicating charge transfer from the substrate. It is shifted down by about 1 eV with respect to that of the free graphene, in good agreement with the experiments.[11,16] The metallic graphene-Ru interface is in agreement of the metallic bonding as shown in Fig. 2(b). It can be seen that the electronic structure of the second graphene layer is rather similar to that of the free graphene, indicating that the incommensurance almost does not affect the electronic states of the second layer. Since the states near the Fermi level are of π character, they are closely related to the electronic states around Dirac point K. The resemblance between the PDOS of the second graphene layer and the free graphene, especially at the Fermi level, implies that the K point related striking properties of the free graphene will also be largely maintained in the second graphene layer on Ru. The bond length, interlayer spacing and electronic structure of the second graphene layer agree with those of the free graphene, showing that it is largely decoupled from the substrate.

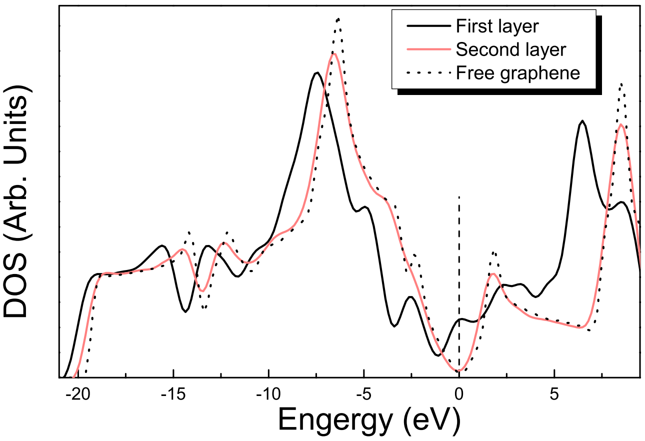

FIG. 4. (Color online) The partial densities of states of the central C ring in the first (black) and second (salmon) graphene layers. The DOS of the free graphene layer is also shown (dotted). The dashed line indicates the Fermi level, which is taken as zero.

IV. CONCLUSIONS

In conclusion, we have studied graphene monolayer and bilayers on Ru(0001). It is found that the simulated STM images of the strongly corrugated graphene/Ru cannot reproduce the observed bias dependence of STM images. Graphene/Ru prefers being quasiperiodic and nearly flat. The graphene monolayer is metallically bonded to Ru. Its π states obtain electrons from the substrate while its σ bonds lose electrons and hence are weakened and stretched. The second graphene layer is incommensurate with the first one. A new moiré structure is found between the graphene bilayers with more C atoms in the second layer per unit area. While the electronic states of the first graphene layer are shifted down by about 1 eV, the electronic structure of the second one resembles that of the free graphene. The second graphene layer is also found to have small corrugations due to the incommensurance with the first one.

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