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Effect of strain on geometric and electronic structures of graphene on a Ru(0001) surface*

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The atomic and electronic structures of a graphene monolayer on a Ru(0001) surface under compressive strain are investigated by using first-principles calculations. Three models of graphene monolayers with different carbon periodicities due to the lattice mismatch are proposed in the presence and the absence of the Ru(0001) substrate separately. Considering the strain induced by the lattice mismatch, we optimize the atomic structures and investigate the electronic properties of the graphene. Our calculation results show that the graphene layers turn into periodic corrugations and there exist strong chemical bonds in the interface between the graphene $N \times N$ superlattice and the substrate. The strain does not induce significant changes in electronic structure. Furthermore, the results calculated in the local density approximation (LDA) are compared with those obtained in the generalized gradient approximation (GGA), showing that the LDA results are more reasonable than the GGA results when only two substrate layers are used in calculation.

Keywords: first-principles calculations, graphene, strain, electronic structure
PACC: 7320A, 0630M, 6820

1. Introduction

Organic nanostructures on metal surfaces with novel physical properties have been widely investigated because of their promising applications in optical and electronic devices.[1−7] Recently, graphene consisting of a single graphite layer has aroused great interest in scientists in a number of fields, such as materials science, condensed-matter physics, chemistry and so on, due to its exceptionally high crystallinity and novel electronic properties.[8] The successful fabrication[9−15] of single layer graphene has aroused new interest in its physics[16,17] and potential application.[18−21] However, owing to its intrinsic electronic property, i.e. zero band gap semi-metal, minimum conductivity prevents its practical application in electronic devices.[22] Previous studies indicated that the electronic structure of graphene could be tailored through an intrinsic spin-orbit coupling,[23] external electric field,[1] chemical doping[24] or substrate-induced mirror symmetry breaking,[25] separately. Recently, monolayer graphene films have been grown on metal surfaces with lattice mismatch resulting in the moiré pattern and forming an $N \times N$ superlattice.[9−11,26−30] It was reported that the suspended graphene exploited from graphite was not strictly two-dimensional but rather an intrinsic corrugation.[31] Hence, strain plays an important role in tailoring the electronic structure of graphene.

The lattice mismatch between the graphene and the Ru(0001) surface is about 9.1%. Thus, every ten ruthenium lattices match eleven graphene periodicities. Experiment found that eleven ruthenium lattices matched twelve graphene periodicities.[9] However, it is well known that this type of moiré pattern is too large for first-principles calculation. In order to have an insight into the influence of strain on the graphene monolayer, three models denoted as 5–6, 6–7 and 7–8, are investigated in the present study, where m–n represents that $n \times n$ carbon periodicity matches $m \times m$ ruthenium periodicity, inducing strain of 8.3%, 5.7% and 3.8%, respectively. It is found that the graphene layer forms a strong chemical bond with the ruthenium substrate. The simplified structures with smaller strain have similar properties to those

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of experimental superstructures. It is also found that different exchange correlation functionals may lead to different results.

2. Computational details

In the present paper, the density functional theory (DFT) calculations were performed by using the Vienna *ab initio* simulation package (VASP).[32] The local density approximation (LDA)[33] was used for the exchange-correlation functional. The electron–core interactions were represented in the projector augmented wave (PAW) approximation[34] and the energy cut-off for the plane-wave basis was set to 400 eV. Periodic slabs containing a two-layer ruthenium substrate and a graphene monolayer asymmetrically adsorbed on one side were used to model the system of graphene overlayers on the Ru(0001) substrate. To ensure that the interaction between the periodic slabs through vacuum is negligible, the slabs were separated by a 16 Å vacuum gap. In geometry optimizations, the adsorbate and the topmost metal layer were allowed to relax until the forces acting on relaxed atoms were less than 0.01 eV/Å. In total energy calculations, a strict k-sampling convergence criterion with an energy difference smaller than 10 meV was employed in the two-dimensional irreducible Brillouin zone (IBZ). The adsorption energy is defined as the difference between the energy of strained graphene on the surface and the sum of the energy of the strained pristine graphene and the energy of bare surface, i.e. $E_{\rm ad} = E_{\rm tot} - (E_{\rm g} + E_{\rm s})$.

To simulate the strained pristine graphene in the absence of the substrate, the graphene layer is preserved and the ruthenium substrate is removed. Here we still denote the three strained pristine graphene systems as 5–6, 6–7 and 7–8 for convenience. A few carbon atoms were initially lifted from the plane of a planar graphene monolayer. After relaxation, a periodic corrugation was introduced into the graphene monolayer (right column in Fig.1). For the adsorbed system, a planar graphene monolayer was placed on the substrate, then the corrugated graphene was obtained due to the periodic potential of the Ru(0001) surface (left column in Fig.1).

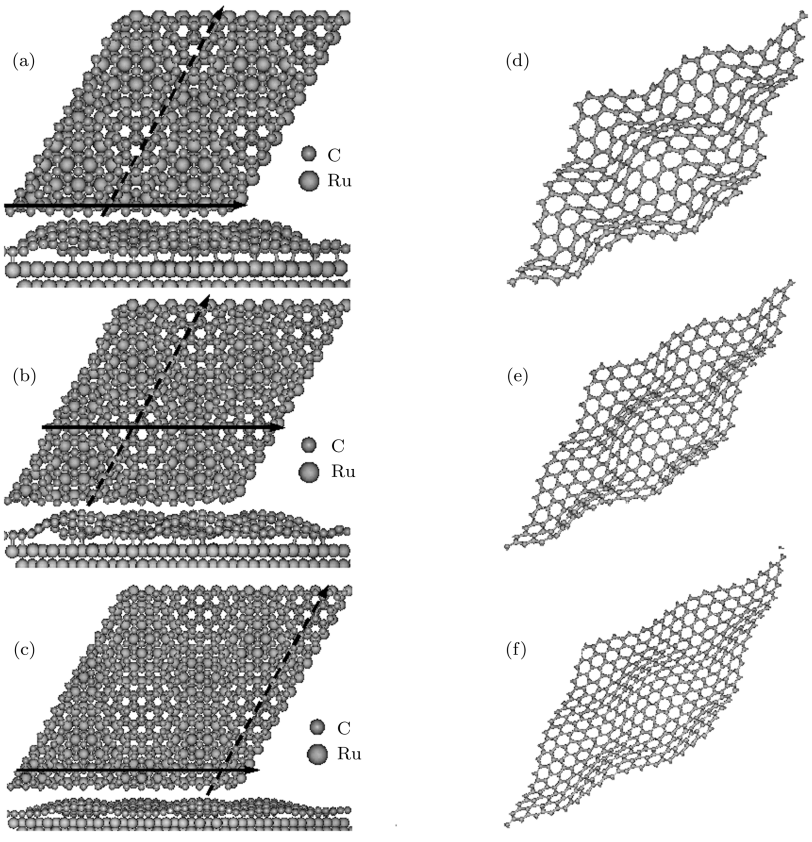


Fig.1. Schematic illustrations of strained graphene monolayer on the Ru(0001) surface (left column) and pristine strained graphene (right column) under compressive strain, where all the panels show the corrugation of graphene.

3. Results and discussion

Table 1 shows the vertical displacements of the graphene monolayer on the Ru(0001) substrate and the pristine graphene after structural optimizations as schematically illustrated in Fig.1. The pristine graphenes of 5–6, 6–7 and 7–8 systems turn into periodic corrugations in order to release the in-plane stress. With the strain decreasing in the sequence of 5–6, 6–7 and 7–8, the vertical distance between the highest carbon atom and the lowest carbon atom decreases. The carbon–carbon bond lengths fall in the range 1.33–1.47 Å, similar to those in the π-systems, revealing no significant change in bond length. When graphene is adsorbed on the substrate, the corrugation of the strained graphene is affected by the periodic potentials of the substrate. With lattice mismatch decreasing in the sequence of 5–6, 6–7 and 7–8, the vertical distance between the highest carbon atom and the lowest carbon atom also decreases. In this way, the vertical distance between the lowest carbon atom and the plane of the first ruthenium atom layer decreases.

Table 1. Optimized structures of the strained graphene/Ru(0001) and pure strained graphene. cl(C–C) is the distance between the highest carbon atom and the lowest carbon atom in pure strained graphene without a substrate. p(C–C) and p(C–Ru) are the distance between the highest carbon atom and the lowest carbon atom, and the distance between the lowest carbon atom and the first layer of ruthenium atoms in graphene/Ru(0001) respectively. $E_{\rm ad}$ is the adsorption energy.

model	cl(C–C)/Å	p(C–C)/Å	p(C–Ru)/Å	$E_{\rm ad}$/eV
5-6	2.821	2.801	2.075	-2.75
6-7	2.923	2.876	1.751	-3.92
7-8	2.537	2.073	1.495	-2.42

To gain insight into the influence of compressive strain on the electronic structure of graphene, the band structures along high symmetry lines of the corrugated pristine graphene were calculated, and the results are shown in Fig.2. Due to band folding, the Dirac point, which connects the valence and the conduction band on the Brillouin zone edge, shifts to the Gamma point in the 5–6 pristine graphene. Corrugation resulting from strain exerts a great influence on the electronic structure of pristine graphene. A comparison between the 6–7 system and the 7–8 system shows obviously that the slopes of the π and π^* bands decrease and the coupling between the σ and σ^* bands declines along the $K \rightarrow G$ direction in the IBZ, when less strain, i.e. less corrugation, is introduced.

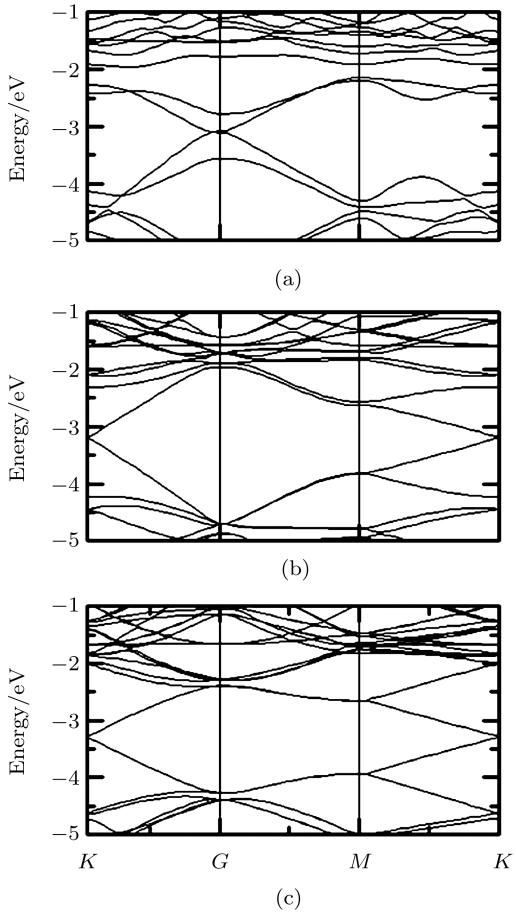


Fig.2. Band structures of 5–6 (a), 6–7 (b) and 7–8 (c) pristine strained graphenes, where the K point of the 5–6 model shifts to the G point due to band folding.

We also calculated the densities of states (DOSs) of the pristine graphene and the graphene monolayer on the Ru(0001) surface. As shown in Figs.3(a), 3(b) and 3(c), the DOSs of pristine graphenes 5–6, 6–7 and 7–8 show V-shape features near the Fermi level, similar to the linear dispersion of pure flat graphene, indicating that the pristine graphene is a semimetal. Interestingly, we observe several round steps near $\pm$0.35 eV and $\pm$ 0.7eV (marked by solid arrows in Figs.3(a), 3(b) and 3(c)), which are not present in free flat graphene.[22] These round steps originate from the corrugations of the graphene sheets. For the graphene monolayer on the ruthenium substrate, *d*-orbital type peaks are clearly seen in the vicinity of the Fermi energy in all three systems (Figs.3(d), 3(e) and 3(f)). The DOS of a graphene monolayer on a substrate reveals that the interface is metallic, indicating that there exists a charge transfer between the strained graphene and the substrate. To determine the charge

transfer direction, we calculated the work functions of the 5–6, 6–7 and 7–8 systems. We found that the work functions of these systems were around 4.8 eV and showed negligible variation, despite different lattice mismatches. Its comparison with the calculated work function of 5.1 eV for clean Ru(0001) indicates that the charge transfers in the direction from the ruthenium substrate to graphene monolayers, leading to the formation of negative interfacial dipoles.

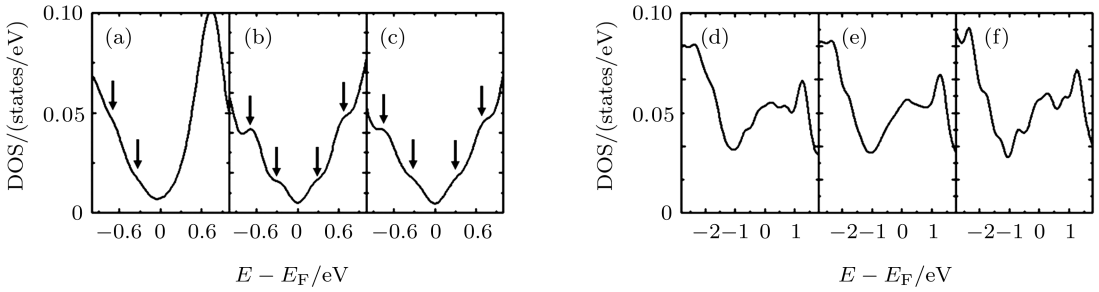


Fig.3. DOSs of configurations 5–6 (a, d), 6–7 (b, e) and 7–8 (c, f), where panels (a), (b) and (c) represent the total DOSs of strained pristine graphene and panels (d), (e) and (f) indicate the calculated total DOSs of graphene/Ru(0001); all the DOSs are shifted to the Fermi energy and averaged to each atom of the whole system and the solid arrows indicate the several round steps near ±0.35 eV and ±0.7 eV.

Of particular interest is the bonding nature of the graphene monolayer on a Ru(0001) substrate. This can be described by a differential charge transfer, which is given by $\Delta\rho_{\mathrm{g/Ru}} = \rho_{\mathrm{g/Ru}} - \rho_{\mathrm{g}} - \rho_{\mathrm{Ru}}$, where $\rho_{\mathrm{g/Ru}}$, ρ_{g}, and ρ_{Ru} are the total electron densities of the graphene monolayer on Ru(0001), pristine graphene and the substrate, respectively. Figure 4 shows the differential charge densities along the [1001] and [0101] directions of the ruthenium substrate. It is clearly seen that the strong bindings indicated by the electron accumulation and depletion areas are located at a minimum vertical separation from the substrate. The charge transfer from the substrate to the graphene overlayer is verified. The adsorption energies of the three systems (as given in Table 1) are more than 2 eV, which suggests that strong chemical bonds may form between the graphene overlayers and the ruthenium substrates. Further analysis reveals that the graphene monolayer has strong couplings with the substrate through $C - \mathrm{p_z}$ and Ru-d_{z^2} orbitals.[35]

It is well known that the LDA and the generalized gradient approximation (GGA) may give incompatible results in DFT calculation of graphite or π–π stacking systems. In order to check the validities of GGA and LDA for the strained graphene systems, we also performed the DFT calculation in the framework of GGA for the 5–6, 6–7 and 7–8 systems either with or without the ruthenium substrate. It turns out that

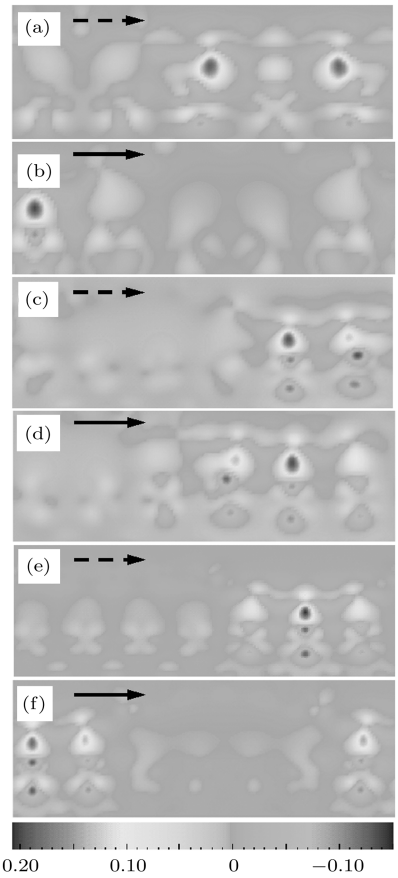


Fig.4. Differential charge transfers of three strained models of 5–6 (a, b), 6–7 (c, d) and 7–8 (e, f), where the slices are indicated with solid and dashed lines as indicated in Fig.1, and are along the [1001] and [0101] directions of the Ru(0001) substrate.

the graphene monolayer only weakly interacts with the substrate and the charge transfers from graphene to substrate in all the systems with a substrate, in contrast to the LDA calculations. In addition, band gaps of pristine graphenes increase with strain increasing in GGA calculations, whereas LDA calculations give a zero band gap. Experimentally, it has been confirmed recently that the graphene monolayer is strongly bonded with the ruthenium substrate and charge transfers from the ruthenium substrate to the graphene monolayer,[36] which is consistent with our LDA calculations. We note that the experiments reveal that the ruthenium substrate may be perturbed down to several atomic layers,[36] whereas only two substrate layers were used in our calculations above, suggesting that more substrate layers should be included to eliminate the deviation arising from different exchange-correlation functionals. We also find that LDA functionals give better results when two substrate layers are used in Ru–graphene systems.

4. Conclusions

We have investigated the superstructures of a graphene monolayer on a Ru(0001) substrate and pristine graphene under different compressive strains by using the LDA method. The graphene layers are shown to turn into periodic corrugations in these models. Strong chemical bonds are formed between the sunken areas of graphene and the ruthenium substrate. The charge transfers from the substrate to graphene overlayer. No significant difference in electronic property among these strained models is observed. More reasonable results are obtained by using the LDA method than by using the GGA method when two substrate layers are used.

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