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Bilayer graphene films over Ru(0001) surface: Ab-initio calculations and STM images simulation

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ABSTRACT

With the aim of better understanding recent experimental results, we performed density functional theory calculations (DFT), including van der Waals interactions, on bilayer graphene over a Ru(0001) surface. Two stacking sequences (*AB* and *AA*) for bilayer graphene were considered and compared with monolayer graphene. For each case relaxed atomic positions, calculated STM images and density of states were obtained and these are discussed in detail. Our results suggest that Moiré patterns of graphene over a Ru(0001) surface have a remarkable electronic influence, whose origin is the coupling of graphene layers and the Ru(0001) surface. Additionally, we found that atomic lattice observed by STM on such Moiré patterns is related with stacking sequence of bilayer graphene.

1. Introduction

Two dimensional (2D) materials are currently attracting considerable scientific and technological interest [1]. From the scientific point of view, they bring the opportunity to test diverse theories on a distinct dimensionality [2–4], while their corresponding electronic structure properties suggest several technological applications [5–7].

Among two dimensional materials, the most widely studied to date has been a stable monolayer of graphite: graphene. Graphene can be obtained from highly oriented pyrolitic graphite (HOPG), resulting in a 2D structure formed exclusively by carbon atoms ordered in a honeycomb lattice. As HOPG is a very common sample in scanning tunneling microscopy (STM) and Raman spectroscopy laboratories, several of its electronic and phononic properties have been reported mainly from these experimental techniques [8–13]. At the same time, from a theoretical point of view, a single graphene layer and few graphene layers are tractable by means of computational methods involving tight binding and/or density functional theory (DFT) [2,14–16].

In the same context, graphitic structures adsorbed on metal surfaces have been reported [17,18], while further investigations have shown that these structures can consist of few graphene layers, or even monolayers [19]. Nowadays, it is well known that the electronic properties of graphene are strongly modified when it rests on another graphene layer [20] or on a Ru(0001) surface [18,21–23]. As a counterpart, graphene adsorbed on a boron nitride substrate showed electronic properties comparable to freestanding graphene [24]. Thus, as the substrate plays an important role in the electronic properties of graphene, the scientific interest for few graphene layers adsorbed on different surfaces has experienced a rapid increase in recent years [25–37]. In particular, the existence of two distinct phases of bilayer graphene (BLG) on Ru(0001) could be very interesting (due to their different electronic properties), and according to experimental results reported recently [31], the first layer could be used as a template to grow different phases of bilayer graphene.

Motivated by experimental observations, this paper presents a theoretical study on the two stacking sequences (*AB* and *AA*) of bilayer graphene over the Ru(0001) surface. For greater clarity the paper has been organized as follows: details of DFT calculations are given in Section 2; comparison of calculated STM images for monolayer and bilayer grahene with experimental observations, as well the main theoretical results for BLG is presented in Section 3; main conclusions are summarized in Section 4.

2. Calculation method

In order to mimic the Ru(0001) surface, a three-layer unit cell was modeled. To model the Ru(0001) surface we fixed the Ru-bulk lattice constant and the atomic positions in the first Ru-bulk layer. As graphene on Ru forms a surprisingly large unit cell, 10 × 10 Ru units were necessary to accommodate 11 × 11 bilayer graphene units: graphene (11 × 11) on Ru (10 × 10). Therefore, the mismatch between Ru bulk and graphene lattice vectors is 0.02 Å. Two stacking sequences for graphene layers were considered: *AA* and *AB*, each with configuration having a corresponding unit supercell composed of 784 atoms. Monolayer graphene over Ru(0001) was also considered, so that we validated

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our results by comparing them with previous experimental reports. In this last case the unit supercell was composed of 542 atoms.

For these models we performed DFT calculations using the SIESTA *ab initio* package [38], which employs norm-conserving pseudo-potentials and localized atomic orbitals as the basis set. Double-ζ plus polarization functions were used under the generalized gradient approximation (GGA) for the exchange correlation potential [39]. All structures were fully relaxed until the atomic forces are smaller than 0.05 eV/Å. We have considered super-cells with periodic boundary conditions. The Brillouin zone was sampled employing only the Γ point; however, we checked the convergence of total energy employing a Monkhorst–Pack mesh of $3 \times 3 \times 1$. For both BLG stacking sequences we have performed calculations including van der Waals (vdW) interactions, using the exchange–correlation potential optB88-vdW [40] which has been successfully applied to graphene over Ni(111) [41]. For monolayer graphene we performed two additional calculations: (a) including vdW correction and (b) considering a rigid flat model for the graphene monolayer to elucidate the effects of atoms relaxation on STM image.

Theoretical STM images were obtained using the code *STM* 1.0.1 (included in the SIESTA package). This code uses the wave functions generated by SIESTA on a reference plane and extrapolates the values of these wave functions into the vacuum. For the following results the reference plane is 1 Å above the top carbon atom so that it is sufficiently close to every carbon atom and the charge density is large and well described. As images were generated under the Tersoff–Hamann approximation [42], the states contributing to the tunneling current lay in the energy window $[E_F - eV_{bias},\ E_F]$, with E_F being the Fermi energy. Data visualization was possible using the WSxM 5.0 freeware [43], and Gaussian smoothing was applied to obtain the final STM images.

Larger unit cells, graphene (12×12)/Ru(11×11) or graphene (25×25)/Ru(23×23), have been reported experimentally and theoretically [26,28,33,37]. However, with the aim of reducing the high computational costs required to include vdW corrections and due to the good agreement with experimental data, we have restricted to the graphene (11×11)/Ru(10×10) unit cell. This super cell has been employed in a previous work [44] to show that vdW interactions reduce by 25% the corrugation of moiré pattern.

3. Results

3.1. Monolayer graphene

Fig. 1(a) and (b) shows the relaxed atomic positions of a monolayer graphene over the Ru(0001) surface. We found protrusions or mounds in the graphene layer forming a superstructure, periodicity of which is 27.45 Å. The maximum height difference among carbon atoms (or mound height) is 1.62 Å; nevertheless it reduces to 1.41 Å, by including vdW corrections (see Table 1). Thus, as stated by Wang and Bocquet [29], this result confirms the significant role played for dispersive forces. Mound heights calculated here are very close to those values calculated in Refs. [23] and [29] (1.5 Å and 1.31 Å respectively), and close to the value 1.16 Å, which was recently calculated in Ref. [33]. Moreover, the mound height calculated here presents a good agreement with experimental values reported elsewhere: 1.5 Å [34] and 1.2 Å [35].

A calculated STM image ($V_{bias} = 1.5$ V at constant height mode) for this system [Fig. 1(c)] shows the current maxima (bright zones) over protrusions. As reported from STM measurements [21,25,26,30,32,35,36], calculated images reproduce the main experimental characteristics: on bright mounds all carbons are resolved; there are two inequivalent tunneling current minima, where only one of the two atoms in the graphene unit cell is resolved. According Wang and Bocquet [29], such current minima inequivalence can be explained by different symmetric registries of C pairs with respect the Ru surface.

A line profile was performed along the highlighted segment in Fig. 1(c) (see inset), and it shows that tunneling current increases roughly 18 times when the STM tip goes from a minimum to a maximum. Such an increase may not be attributable exclusively to graphene layer deformation: considering that reference plane for a calculated STM image is 1 Å above the topmost carbon atom and 2.6 Å above the bottom one, it is expectable that tunneling current increases only 2.6 times. As occurs for graphene over different substrates [13,16], these results suggest that the STM tip also detects modifications in the electronic structure. To support this last statement we calculated STM images for several bias voltages and, by assuming that depressions in current lead to proportional approximation of the STM tip to the surface, we could have an estimation of the corrugation detected experimentally. Therefore, calculated corrugation amplitude for several bias voltages is summarized in Table 2. This fact agrees with experimental data obtained independently [26,27,44] which show a dependence on bias voltage applied during experiments. However, these calculations do not show a bright areas shifting as reported by Pan et al. [26].

On the other hand, lattice constant of calculated STM image (27.45 Å) differs from the value obtained experimentally (30 Å) [26,35], because the unit cells which describe more precisely this parameter are graphene (12×12) on Ru (11×11) [18,21] or graphene (25×25) on Ru (23×23) [22,33]. Nevertheless, DFT calculations employing these enormous unit cells produce even lower mound heights (1.14 Å in Ref. [33]). Additionally, calculated STM images for a rigid graphene

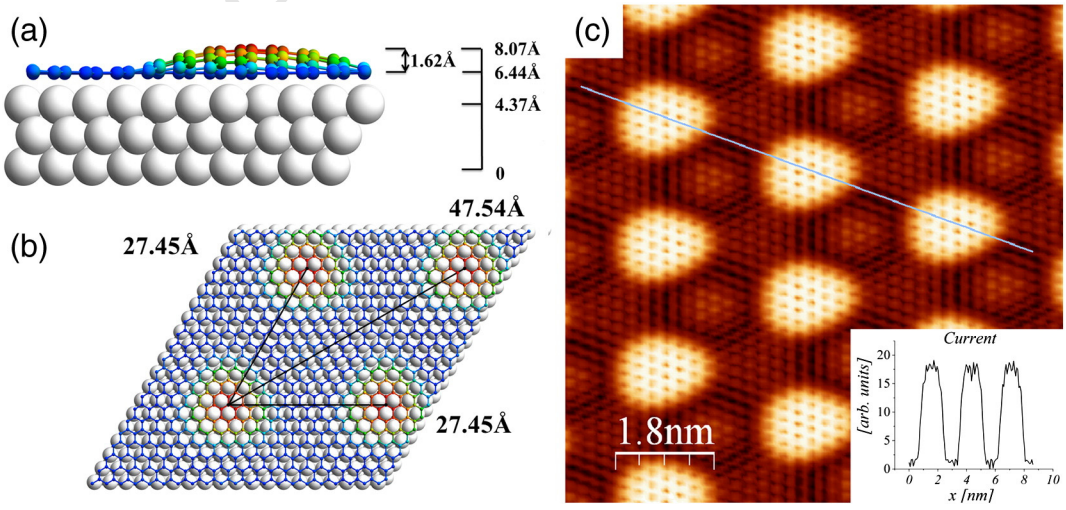

Fig. 1. (Color online) Side view (a) and top view (b) of relaxed atomic positions of monolayer graphene over the Ru(0001) surface. Ru atoms appear in gray, while C atoms are colored according to their height over the Ru surface. (c) Calculated STM image (constant height mode at $V_{bias} = 1.5$ V) and its corresponding line profile (inset).

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