Periodicity, work function and reactivity of graphene on Ru(0001) from first principles

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New Journal of Physics 12 (2010) 043041 (15pp)
Received 29 September 2009
Published 23 April 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/4/043041

Abstract. Using density functional theory (DFT), a detailed analysis of the energetic and electronic properties of monolayer graphene on Ru(0001) was performed. Firstly, we demonstrate that the corrugated \((12 \times 12) C/(11 \times 11) Ru\) structure is an absolute minimum among smaller and larger commensurabilities. Secondly, we show that the reduced work function originates from the charge depletion in the graphene skeleton states at bonded carbon atoms, in contrast to the assumed n-doping of \(\pi\) states. We further propose that the higher-lying regions of the graphene layer form an array of electronically disconnected nanographene islands. Finally, we explore the adsorption properties of this template with respect to metals by comparing the adsorption of Au and Pt single atoms. A 1.1 eV (0.7 eV) preference is found for Au (Pt) atop adsorption in the low region with 0.2–0.3 eV selectivity for the (hcp, top) locations, in agreement with recent experiments on Pt clusters.
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1. Introduction

Adsorbed graphene layers on metal surfaces have been known for more than 40 years but have recently attracted a great deal of interest. As one would expect, the very special properties of graphene [1]–[5] are modified by the interaction with the metal surfaces. However, the nature of these interactions, their effects on the electronic properties and geometry of graphene and the surprisingly strong variations between different metals are not fully understood as yet. Graphene has been synthesized on Ni(111) [6], Pt(111) [7], Ir(111) [8], Ru(0001) [9, 10] and other metals (for a recent review see [11]). The epitaxial growth of graphene on metal surfaces is also of interest as a means for preparing very large layers with low defect concentrations.

A particularly well-studied system is graphene–Ru(0001) (g/Ru). Investigations have been performed using density functional theory (DFT) [12]–[14], scanning tunneling microscopy (STM) [9, 10], [15]–[18], low-energy electron microscopy (LEEM) [19]–[21], angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) [18, 22] and x-ray photoelectron spectroscopy (XPS) [23]. It has been demonstrated that the lattice mismatch between graphene and Ru(0001) induces a large moiré superstructure. Graphene is relatively strongly chemisorbed in specific and connected areas of the moiré structure, giving rise to an ordered pattern of physical mounds and valleys. The characteristic conical points at K in the band structure are removed.

There are several open questions connected with theoretical understanding of the graphene–Ru(0001) interface. Which is the most stable periodicity predicted by DFT? To date, two moiré periodicities have been tackled theoretically, a $(10 \times 10)$Ru and a $(11 \times 11)$Ru structure [13, 14], in accord with high-resolution STM data, but a comparative energetic analysis is lacking. Moreover, a recent surface x-ray diffraction (SXRD) experiment has revealed a much larger periodicity, a $(25 \times 25)C/(23 \times 23)$Ru structure [24]. This structure consists of four almost identical subunits, and it is the modulation caused by these subunits that appears as moiré structure in STM. The subunit structure is, of course, not periodic—it would correspond to a $(12.5 \times 12.5)C/(11.5 \times 11.5)$Ru structure—so that we will call it quasi-periodic in the following. The quasi-periodicity only deviates by half a graphene unit cell from a periodic structure. We can therefore analyze the series of periodic moiré structures $(10 \times 10)$Ru, $(11 \times 11)$Ru and $(12 \times 12)$ Ru to estimate the position of the energy minimum of the full structure.
Secondly, how does the charge redistribute in the contact areas? According to the calculations, the chemical bonding can be traced back to charge transfer from d states of Ru atoms to the p\text{z} states of the atop-bonded C atoms [12]. However, this n-doping character of the graphene layer seems inconsistent with the measured lowering of the work function relative to the uncovered Ru [22]. Recently, graphene-induced work function changes have been computed using DFT for Ni, Co and Pd, which interact relatively strongly with graphene, and for Al, Ag, Cu, Au and Pt, which interact weakly by physisorption [25]. For the weakly interacting systems, it has been shown that there is a relatively simple correlation between the charge transfer and the work functions of the separate metal and graphene (plus some ‘chemical correction’). The question arises: How can one understand the work function changes for the strongly interacting systems, for which g/Ru is one example?

Thirdly, what does DFT predict of the g/Ru template properties for metal cluster deposition? One may expect that the mound/valley topography of the moiré structure can be used for growing size-selected clusters of metal atoms, and one interesting example is clusters of Au atoms [26, 27]. Clusters of Pt atoms have already been prepared on g/Ru template [28, 29]. Interestingly, Pt clusters first segregate in the low regions with a marked selectivity for the fcc-moiré locations equivalent to an (hcp, top) C registry. The template property has already been demonstrated by combined experimental and theoretical studies for graphene on Ir(111), on which ordered arrays of Ir clusters are stable up to 500 K [8, 30]. The stability has been explained by a local sp\textsuperscript{3} rehybridization of the initially almost flat graphene (g/Ir belongs to the weakly interacting class), causing pinning of the clusters [31]. A related two-dimensional (2D) material, epitaxial h-BN on metal surfaces [32], has been used to grow Au nanoparticles [33]–[35], which are preferentially trapped in the low regions of the corrugated surface. By investigating the adsorption of single Au and Pt atoms on the strongly interacting, strongly buckled graphene on Ru(0001), we can compare its initial reactivity with flat g/Ir and with the corrugated h-BN/metal templates. This may serve as a guide for the experimentalists to further explore metal growth.

The outline of this theoretical paper is as follows. Firstly, we compare the geometrical structure and the stability of g/Ru for three different periodicities. Secondly, we analyze the computed work function change. Thirdly, we analyze the sigma states of graphene where we find a possible electronic signature of the high regions of buckled graphene. Fourthly, the reactivity of the low region towards atomic adsorption of Au and Pt is quantified.

2. DFT calculations

All calculations were carried out within DFT using VASP package [36]. The generalized gradient approximation in Perdew–Burke–Ernzerhof form (PBE-GGA) [37] was used for the exchange-correlation potential and electron–core interactions were treated in the projector augmented wave approximation [38]. The structural calculations were performed with an asymmetric slab with one layer of graphene on a three-layer Ru slab, separated by a vacuum interspace of 7.5 Å. For this part of the investigation the Brillouin zone was sampled with a single k-point at \Gamma. The graphene layer and the uppermost Ru layer were relaxed until the self-consistent forces reached 0.1 eV Å\textsuperscript{-1}. During the relaxation, the cut-off energy was set to 300 eV. The method of Methfessel–Paxton was used to treat the partial occupancies (0.2 eV smearing width).

The energy decomposition and density of states (DOS) calculations were performed on the relaxed structures with an increased k-mesh (3 \times 3 \times 1) to achieve energy convergence and...
Figure 1. DFT-optimized \((12 \times 12)\)C/\((11 \times 11)\)Ru structure, with the unit cell indicated as a black rhombus. (a) Schematic of the atomic structure. The shading of the C atoms marks their relative heights with respect to the Ru substrate. The topmost first and second layer Ru atoms are depicted in cyan and green, respectively. The colored circles mark different registries of carbon atoms with respect to the Ru(0001) surface, with cyan indicating (Chcp, Ctop), red (Chcp, Cfcc) and green (Cfcc, Ctop) configurations. (b) Oblique view of the C height map relative to the Ru substrate, showing high (red) and low (blue) regions.

enhance the DOS resolution. The charge density redistributions and the electrostatic potential were computed with a symmetric slab approach, a five-layer Ru slab with one graphene sheet on each side, and a vacuum space of 30 Å. In all calculations of adsorbed graphene, the Ru bulk lattice constant was kept fixed at the calculated value of the uncovered metal \((a = 2.724 \text{ Å}; b = 4.305 \text{ Å})\), in good agreement with experimental values \((a = 2.706 \text{ Å}; b = 4.28 \text{ Å})\).

3. Results

3.1. Energetic analysis

As shown by STM experiments [9], a moiré structure appears when graphene grows on the Ru(0001) surface because of the lattice mismatch. The first DFT computation of the full moiré cell revealed a periodically buckled graphene sheet with varying bonding strength ranging from van der Waals to chemical type. The results published elsewhere [12] are recalled in figure 1. The figure depicts the relaxed atomic structure of epitaxial graphene on Ru(0001) and the
Table 1. Calculated structure parameters for the three moiré periodicities considered. Stretch-g is the relative change of the graphene lattice parameter between the epitaxial and free-standing cases. Corr-g and Corr-Ru are physical buckling values ($z$-projected distances) for the graphene and surface Ru planes, respectively. $d_{eq}$ is the minimum equilibrium separation between the graphene sheet and the metal surface and $\delta$Ru the respective separation between the two topmost metal surface planes.

| Moiré     | (10 × 10)Ru | (11 × 11)Ru | (12 × 12)Ru |
|-----------|-------------|-------------|-------------|
| Stretch-g (%) | 0.3%        | 1.1%        | 1.8%        |
| Corr-g (Å)   | 1.62        | 1.51        | 1.44        |
| Corr-Ru (Å)  | 0.05        | 0.05        | 0.04        |
| $d_{eq}$ (Å) | 2.23        | 2.22        | 2.24        |
| $\delta$Ru (Å)| 2.07        | 2.08        | 2.07        |

corresponding 3D height map of the carbon atoms. The corrugation of the graphene layer is 1.5 Å, and the minimum distance between C and Ru is 2.2 Å, giving rise to two distinct domains on the graphitic surface: the *high* and *low* regions. On the *high* regions, here centered at the corners of the rhombic unit cell, the two C atoms per graphene unit cell are located above the fcc and hcp hollow sites of the Ru surface. In the *low* regions, one of the two C atoms occupies (or sits very close to) a top site, whereas the adjacent C atom occupies (or sits very close to) the hcp site in the left half of the unit cell (blue circle in figure 1), or the fcc site in the right half (green circle in figure 1). The buckling of the first Ru layer (not shown) is 0.05 Å.\(^4\)

In addition to the considered (12 × 12)C/(11 × 11)Ru periodicity in figure 1, there has been a collection of periodicity measurements reported in the literature for this system. In low-energy electron diffraction (LEED) experiments, periodicities (with respect to Ru) ranged from 11.6 ± 0.2 \([9]\) to 11 \([16]\), to 10.8 ± 0.3 \([19]\), and 9 \([39]\). Atomically resolved STM indicated periodicities of 11 \([9, 16]\) and 10 \([10]\). The most precise value from experiment is a (25 × 25)C/(23 × 23)Ru structure \([24]\). It correlates with the other, roughly half as large, periodicities as it consists of four almost identical subunits, corresponding to an 11.5 quasi-periodicity. To account for these variations in the experimental data, we have calculated two additional moiré structures within the same theoretical settings as for the model of figure 1, namely an (11 × 11)C/(10 × 10)Ru and a (13 × 13)C/(12 × 12)Ru structure. Tables 1 and 2 summarize the structural results and the energetic analysis.

From the (10 × 10)Ru to the (11 × 11)Ru to the (12 × 12)Ru structure, the strain (Stretch-g) with respect to the calculated, free-standing graphene increases from 0.3 to 1.1 to 1.8%. The data (table 1) show that the buckling of the graphene layer (Corr-g) is similar in all three cases, and that there is a non-negligible distortion of the relaxed Ru layer. Considered in detail, the graphene buckling (Corr-g) decreases when the tensile strain (Stretch-g) increases,

\(^4\) In a more expanded calculation (cut-off energy 400 eV, two Ru layers relaxed in a four-layer slab Ru), the first layer Ru buckling increased to 0.09 Å. The (11 × 11)Ru structure has also been computed with the LDA functional, and Corr-g = 1.75 Å, $d_{eq}$ = 2.12 Å were obtained for the geometry parameters. Since these values exhibit the typical trend of LDA versus GGA functionals, namely to give a shorter bond to the metal and thus a larger corrugation, our discussion only focuses on GGA-PBE results.
Table 2. Decomposition of the graphene adsorption energy per unit cell for three periodicities of the moiré structure. Stretching energy-g is the energy cost to stretch flat graphene to match the moiré periodicity. Distortion energy is the deformation energy of graphene (-g) and of the Ru slab (-Ru) when the two surfaces are brought into contact. Ncontact C is the number of C atoms with Ru–C bond length smaller than 2.5 Å.

| Moiré         | (10 × 10)Ru | (11 × 11)Ru | (12 × 12)Ru |
|---------------|-------------|-------------|-------------|
| \(E_{\text{Adsorption}}\) (eV)     | −2.2        | −3.9        | −2.7        |
| Stretching energy-g (eV)            | 0.0         | 1.5         | 5.8         |
| Distortion energy-g (eV)            | 3.3         | 4.2         | 5.4         |
| Distortion energy-Ru (eV)           | 0.3         | 0.4         | 0.5         |
| \(E_{\text{Interaction}}\) (eV)    | −5.8        | −10.0       | −14.4       |
| Ncontact C                             | 69          | 96          | 108         |

indicating that by horizontally stretching the graphene layer one at the same time lowers its vertical deformation. This is qualitatively what one would expect if one considers the graphene layer as a 2D array of atoms coupled by harmonic springs that is deformed by a normal force. On the other hand, the minimum graphene–Ru distance (\(d_{\text{eq}}\)) and the minimum Ru–Ru layer distance (\(\delta_{\text{Ru}}\)) are almost independent of the moiré periodicity.

The data of table 2 are used to compare the energetics of the three structures. The adsorption energy and interaction energy per unit cell are defined as

\[
E_{\text{Adsorption}} = E(g + Ru) - E(g) - E(Ru),
\]

\[
E_{\text{Interaction}} = E(g + Ru) - E'(g) - E'(Ru),
\]

where \(E(g + Ru)\) is the total energy of the optimized graphene–Ru(0001) structure, \(E(g)\) is the energy of an isolated unstretched graphene sheet and \(E(Ru)\) is the energy of the bare Ru surface. \(E_{\text{Adsorption}}\) thus contains all chemical and elastic energy contributions when isolated graphene attaches to the Ru(0001) surface. \(E'(g)\) is the energy of an isolated, but distorted and stretched graphene sheet and \(E'(Ru)\) is the energy of a bare, but distorted Ru surface. \(E_{\text{Interaction}}\) can thus be viewed as the pure chemical energy contribution when an already properly deformed graphene sheet and Ru are brought into contact. The decomposition of \(E_{\text{Adsorption}} = E_{\text{Interaction}} + \text{Stretching energy-g} + \text{Distortion energy-g} + \text{Distortion energy-Ru}\) thus allows us to analyze the contributions of the individual energies. (To transform the energies in table 2 into energies per C atom the data in the three columns have to be divided by 242, 288 and 338 C atoms, respectively. However, this leaves all trends unchanged.)

As the data in table 2 show, the adsorption energy \(E_{\text{Adsorption}}\) is maximum for the (11 × 11)Ru periodicity (−3.9 eV).\(^5\) This energy explains the overall stability of the moiré structure as a result of competing components. Bringing graphene and Ru into contact induces chemical bonds between Ru and C atoms with significant orbital hybridizations as proposed by DFT calculations [12] and later verified by XPS [23] and ARUPS measurements [22]. Experimentally, the Ru–C chemical bonding is indicated by a large downshift of the π-graphene

\(^5\) This lower value, as compared to −6.7 eV [12] and −6 eV [14] from two previous papers, results from the finer \(k\) mesh applied in the present calculations.
states in the band structure and by the removal of the Dirac points. The simultaneous downshift of the $\pi^*$ band results in partial occupation of antibonding states and thus in weakening of the C–C bonds.

Hence, the most stable structure results from a balance between Ru–C bonding and C–C bonding. The strength of the Ru–C bonding is entirely expressed by the interaction energy $E_{\text{Interaction}}$, which increases as the periodicity increases from $(10 \times 10)$Ru to $(12 \times 12)$Ru. This increase can be understood by the number of C atoms per unit cell that are in close contact with Ru (Ncontact C) that shows the same behavior. Ncontact C is, somewhat arbitrarily, defined as the number of C atoms at a distance less than 2.5 Å, but the trend remains the same even if this threshold distance is defined differently. When the height modulation of the graphene (Corr-g) becomes smaller with increasing strain, more C atoms come into close contact distance to the Ru atoms. This increasing bonding strength is countered by the increasing stretching energy-g and the increasing distortion energy-g, whereas the distortion energy-Ru remains almost constant. The stretching energy-g shows a strong, higher than linear increase with strain, in good agreement with the picture of harmonic springs connecting the C atoms. The most stable $(11 \times 11)$Ru periodicity that is connected with a 1.1% strain is thus the result of a compromise between an enhanced chemical bonding compared to the unstretched graphene and the stretching energy of the (horizontally) very stiff graphene sheet. The actual $(23 \times 23)$Ru periodicity that consists of four $(11.5 \times 11.5)$ subunits still fits well into this picture.

Finally, we would like to comment on the actual strength of the graphene–Ru interaction quoted in Table 2. When one considers $E_{\text{Interaction}}$ per C atom for the $(11 \times 11)$Ru periodicity, one finds 35 meV (when one counts all C atoms in the unit cell), 104 meV (when one counts only the Ncontact atoms) and 208 meV (when one counts only the actually binding, top-site C atoms of the Ncontact atoms). These values appear relatively small considering the strong electronic modifications of the graphene $\pi$ states. As first commented for the case of a prototype aromatic molecule like PTCDA on Ag(111) [40], the short C–Ru bond may have a dual character: it is an electronically active bond displaying massive charge transfer but a mechanically weak anchor as suggested by the modest energies involved.

3.2. Dipole moment and work function change

ARUPS measurements [22] and DFT calculations [12] have recently shown that the electronic properties of graphene are strongly altered at the g/Ru interface with respect to the separate systems. These changes are in marked contrast to the g/Ir case [41]. The characteristic conical points at $\bar{K}$ are destroyed and a coupling between $\pi$ states of graphene and d bands of Ru is evidenced. The graphene overlayer becomes n-doped as a result of a downshift of the $\pi$ states, in agreement with other studies [14]. The charge transfer between graphene and Ru substrate results in the formation of an interface dipole, modifying the work function of the graphene-covered metal. The measured work function of g/Ru with UPS is 3.9 eV [22] (in older work a value of 4.5 eV was found [42]), i.e. distinctly lower than the 5.4 eV measured for clean Ru(0001) [42]. The work function changes amount to a decrease of $\Delta \phi = -1.5$ and $-0.9$ eV, respectively.

Usually, a work function decrease implies adsorbate-to-substrate charge transfer, which, in the present case, would result in a p-doped graphene overlayer, in contrast to the experimental findings. This apparent contradiction between adsorbate charging and the sign of the work function change has been recently investigated theoretically for the case of N adatoms on
We here follow the same theoretical strategy by computing the plane-integrated difference electron density $\Delta n(z)$ in order to visualize the electron redistribution upon formation of the interface. $\Delta n(z)$ is defined as

$$\Delta n(z) = \int_{0}^{X} \int_{0}^{Y} \Delta n(x, y, z).$$

(3)

$\Delta n(z)$ is then used to calculate $\Delta \mu(z)$:

$$\Delta \mu(z) = (z - s) \Delta n(z),$$

(4)

$\Delta \mu(z)$ can be viewed as an incremental dipole moment created by the incremental 2D charge $\Delta n(z)$ at a given distance in front of the surface. $s$ is the position of the Ru surface on the $z$-axis. The surface dipole moment is then given by

$$\mu = \int_{0}^{Z/2} \Delta \mu(z) \, dz,$$

(5)

where $X$, $Y$ and $Z$ are the cross sections of the supercell in the three dimensions.

For these calculations, a symmetric configuration was considered, with a graphene layer on both sides of the slab. The surface dipole $\mu$ is obtained by integrating $\Delta \mu(z)$ in the $z$-direction from the center of the slab ($z = 0$) to half the length of the unit cell ($z = Z/2 = 25 \text{ Å}$). A value of $-0.29 \text{ D per 1} \times 1 \text{ cell}$ was obtained. This dipole moment corresponds to a work function of $\phi = 3.6 \text{ eV}$ or a work function decrease of $\Delta \phi = -1.7 \text{ eV}$, in very good agreement with the recent experimental value.

Figure 2 illustrates the charge redistributions, induced by bringing the graphene layer and the Ru(0001) surface into contact, and the effects on the work function. Figure 2(a) clearly shows that the charge transfer is non-uniform across the moiré structure. The low region displays a chemical interaction, whereas the high region hardly interacts. Zooming-in into the low region (figure 2(b)) reveals details of the chemical interaction (figure 2(b) also shows a top view of this area). Electron accumulation areas (red) are localized on the atop C atoms, resembling $p_z$ atomic orbitals. The maximum of the increased electron density appears at the interspace between C and Ru layers, a direct signature of the covalent bonding between the Ru4d and C2p$z$ orbitals. In contrast, electron depletion areas (blue) appear at the hollow C atoms. This charge is mainly localized within the graphene plane, showing sigma-type character, although it is slightly asymmetric, somewhat closer to the Ru layer. As a result, the vertical positions 1–3 display an oscillating charge character, a $-/+/−$ sequence as one moves from the Ru surface into the vacuum. This qualitative picture also becomes apparent in the plot of the plane-integrated charge $\Delta n(z)$ (figure 2(c)). The planes at 1 and 3 below and above the plane of the low-lying C atoms are negatively charged, the in-between plane (2), close to the low-lying atomic plane, is positively charged. The negative charge at planes 1 and 3 is in agreement with the n-doping of the $\pi$ system, observed as an energy downshift in ARUPS [22]. However, the sequence of charge layers with alternating polarity shows that the redistribution process is much more complex. The incremental dipole moment $\Delta \mu(z)$ (figure 2(c)) closely follows this charge distribution. Planes 1 and 3 lead to a positive and plane 2 to a negative $\Delta \mu(z)$. By plotting the integrated dipole moment as a function of the upper integration limit, we can thus directly analyze the contributions of the individual charges. Figure 2(d) shows the result, after conversion into $\Delta \Phi$. One can see that $\Delta \Phi$ reaches a plateau at a distance of $z = 10 \text{ Å}$ at a

6 The relationship between $\mu$ and $\phi$ is $\phi = (e/\epsilon_0)(\mu/\Lambda)$ with $\Lambda$ being the surface area [45].
Figure 2. (a) Charge density difference map of graphene on Ru(0001) along the diagonal of the moiré unit cell. Red and blue isosurfaces correspond to $\pm 0.03 \text{eÅ}^{-3}$, indicating electron accumulation and depletion regions, respectively. (b) Detail of the hcp-low region of (a), with the side (left) and top (right) views. The charge densities were visualized with VESTA software [44]. (c) Plane-integrated difference electron density $\Delta n(z)$ (dashed curve) and plane-integrated incremental dipole moment $\Delta \mu(z)$ (bold curve) as functions of $z$, the vertical position relative to the center of the five-layer metal slab. $z = s$, indicated by a dotted line, corresponds to the surface plane. Numbers 1–3 correspond to the positions in (b). (d) Work function change obtained by integration of the $\Delta \mu(z)$ curve as a function of $z$ with respect to the bare Ru surface, i.e. $\Delta \phi(z) = \phi(z) - \phi(\text{Ru})$.

work function decrease of 1.7 eV. This value remains constant up to the end of the integration at $z = 25 \text{Å}$, so that the main effect directly occurs in the graphene layer. Figure 2(d) clearly shows that the strongest contribution to the decrease comes from the positive charge close
to the sigma states. The negative charge in the $\pi$ system also contributes, but the effect is smaller. The apparent contradiction between the n-doping of the graphene $\pi$ system and the work function decrease is thus resolved by the computation of the integrated dipole moment at various heights above the interface. Interestingly, a similar charge redistribution mechanism has previously been proposed for benzene molecules adsorbed on Ru(0001) \cite{46} to rationalize the large work function decrease of 1.8 eV \cite{47}. This resemblance supports a close relationship between graphene in the low contact regions and adsorbed benzene molecules.

### 3.3. Localized $\sigma$ states of nanographene

As the effect on the work function shows, the sigma states significantly contribute to the electronic structure of the adsorbed graphene. The question therefore arises: How do the sigma states interact with the Ru surface? When a particle physisorbs on a metal surface, its electronic structure remains almost independent of the substrate, and its orbital energies are pinned to the vacuum level. This property has also been found for a layered adsorbate, epitaxial $h$-BN on metal surfaces \cite{48}. In the g/Ru case, this picture applies to the $\sigma$ and 1s states of the C atoms, which should reflect the lack of hybridization with metallic orbitals. Hence, these states are pinned to the vacuum level instead of the Fermi level of the substrate. Due to the potential modulation of 0.5 eV that has been calculated for this system (figure 3(a)), one would expect that $\sigma$ and 1s states from low and high regions exhibit this energy splitting. In XPS experiments, the C 1s line was indeed found to split into two distinct components with 0.60 eV energy separation \cite{23}, in good agreement with our calculations. A way to check for the existence of such an energy splitting by theory is by comparing the projected DOS (pDOS) onto the $p_x$ states of representative C atoms from the low and high regions of the epitaxial graphene. Figure 3(b) shows such data for atom C1 from the high region and for atom C8 from the low region. Qualitatively, the downshift of the $\sigma$ states from the low region relative to the high ones is well reproduced.

More interesting is an additional feature arising from the pDOS analysis, a localized state (sharp resonance marked in yellow) appearing at the high-energy edge for the C1 atom (high region). This state appears largely decoupled from the lower-lying band reflecting the scattering states of graphene. The charge density of this localized state closely resembles that of the highest-lying $\sigma$ molecular state of gas-phase C$_{55}$H$_{18}$ (figure 3). Our current understanding is the following: the high regions, with their higher electrostatic potential, are separated from each other and form an array of zero-dimensional nanographene islands.

### 3.4. Gold and platinum monomer adsorption on g/Ru

In order to investigate the initial chemical reactivity of g/Ru with respect to metal atoms, we have investigated the adsorption of Au and Pt single atoms. The results are compared with the adsorption on the free-standing but corrugated graphene layer. Selected atomic positions along the diagonal of the moiré unit cell were explored, mainly atop C atoms, and the results are shown in figure 4.

First we have considered rigid substrates (filled circles), i.e. the free-standing buckled graphene (black dots) or the g/Ru surface with a geometry unchanged by the Au adsorption and only relaxed the $z$-coordinate of the Au adatom (red dots). Then the Au/g/Ru system was fully relaxed for three specific sites (open red circles) and compared to its analogue with platinum.
(Pt/g/Ru system with open blue circles). On the isolated corrugated graphene, Au adatoms adsorb on C atoms on atop sites with a small adsorption energy (around 100 meV). The flatness of the energy curve as a function of lateral position (full black circles) indicates that Au would easily diffuse over the rough graphitic surface. Hence, the geometrical corrugation has only a minor effect on the adsorption energy. In contrast, adsorption on g/Ru shows an enhanced reactivity of C atoms at the low regions (e.g. on carbon atom C8, see figure 4(a) as compared to the atoms on the high regions. Among all tested sites, the top position on the hcp-bonded C atom C8 is the favorite adsorption site, corresponding to an adsorption energy of almost $-0.7$ eV. When the full relaxation of the graphene overlayer is included (open red circles), the energy increases to $-1.4$ eV for C8. This change is connected with a significant local deformation of the graphene overlayer. The Au atom above C8 pulls the C8 atom up by 0.35 Å, forming an Au–C bond with a bond length of 2.12 Å. Interestingly, this pulling effect is opposite to the effect induced by Ir adatoms on g/Ir(111) [31]. In the g/Ir case, the graphene layer underneath

**Figure 3.** (a) Calculated potential map at 3.8 Å above the topmost C atoms. Two carbon atoms of the low and high regions of the graphene layer are marked with crosses. The molecule C$_{54}$H$_{18}$ can be viewed as a model of the high region part of the graphene. (b) DOS of the sigma states of the graphene overlayer projected on $p_x$ of C1 (red) in the high region and on $p_x$ of C8 (cyan) in the low region, and comparison with the C-averaged $p_x$ state of C$_{54}$H$_{18}$. The Fermi level is set to zero. Insets: band-decomposed charge densities of the sharp resonances marked yellow.
Figure 4. Adsorption energy of a gold atom adsorbed on the rigid buckled graphene overlayer without (black dots) and with (red dots) Ru substrate, as a function of position along the diagonal of the unit cell. Selected atop positions of the Au atom above C atoms are indicated by numbers. For three positions, C1, C8 and C17, the adsorption energies of the fully relaxed Au/g/Ru system (red open circles) are compared to those of the fully relaxed Pt/g/Ru system (blue open circles).

the adsorbed Ir atoms moves closer to the Ir(111) substrate and experiences a local sp²-to-sp³ rehybridization. The difference can be attributed to the different starting configurations, a graphene layer at a large distance from the surface, 3.5 Å, in the g/Ir case, compared to 2.2 Å in the low region in the g/Ru case, and a related, quite different electronic structure. On the other hand, when the Au atom is positioned above C1 of g/Ru (see figure 4(a)), the structure of graphene is not changed, the Au–C bond length is 2.6 Å and the adsorption energy is only 0.26 eV. A free Au atom has a 5d¹⁰6s¹ valence electron configuration, with a net spin of 1. When it adsorbs on a metal surface, charge transfer will usually change the charge state and the spin of the gold atom. Our spin-polarized calculations show that Au above C1 retains a spin of about 0.72, while the spin is totally quenched for Au above C8 as a result of a larger charge transfer.

The energy difference between low and high regions (in both cases atop positions) reaches 1.1 eV. This value is much larger than the 0.2 eV difference calculated for Au adatoms on an FeO/Pt(111) substrate [49] for the various local binding sites. We also found 0.2 eV preference for atop adsorption on C8 (hcp) versus C17 (fcc), which shows that a single Au atom discriminates between carbon atoms on different hollow sites. The findings hold true when replacing Au by Pt on the moiré cell but the interaction is much stronger: the adsorption values (blue open circles) lie now in the range between −2 eV and −3 eV, in excellent agreement with

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recent STM studies [28, 29]. This unequal bonding on different sites of the moiré cell is fully understandable. The C8 atom is positioned on a hollow site of the Ru substrate. It displays a broad and intense electronic state straddling the Fermi level [12], which can be viewed as an unsaturated dangling bond. This strong local variation of the binding energy suggests that g/Ru may be a suitable template for growing all kinds of transition metal clusters selectively in the low regions of the overlayer. The mechanism of this locally enhanced binding is different from binding variations known from nanotubes. When nanotubes are chemically functionalized, the binding energy of radical adsorbates is strongly sensitive to the diameter and thus the local curvature of the nanotube [50]. For g/Ru, the local curvature is much smaller than for nanotubes, and hybridization angles are smaller than 1°. Hence, the enhanced chemical bonding on g/Ru only originates from the lifted equivalence of the two C sublattices due to the chemical interaction with the metallic substrate.

4. Conclusions

Using DFT we have, firstly, explained why the (12 × 12)C/(11 × 11)Ru structure is the most realistic commensurate model to account for the g/Ru interface. This periodicity is the result of a compromise between stronger bonding to the metal for a slightly (1.1%) stretched graphene and a sharply increasing elastic energy for further stretching. The resulting periodicity agrees well with the experimentally observed (11.5 × 11.5)Ru structure [24]. Secondly, we have shed light on the complex charge redistributions at the low regions, where the chemical contact is localized, which result in a work function decrease. We demonstrate that the π system adopts a negative charge, but that the overriding effect is a positive charging of the sigma states of the graphene skeleton. Thirdly, we have proposed a new picture of the high regions of the graphene overlayer. The high regions, where the electrostatic potential is locally higher, are embedded in the low regions where the electrostatic potential is lower. An energetically high-lying σ state of the high region, resulting from this electrostatically induced energy shift, is decoupled from the other scattering σ states at the low regions. The decoupled state is localized both in energy and space, thus resembling a discrete molecular orbital of a nanographene island. Finally, we have explored the adsorption properties of Au and Pt atoms and show that g/Ru may be a good template to accommodate metal adatoms specifically on the hollow C atoms in the low regions.

Acknowledgments

We acknowledge fruitful discussions with Thomas Brugger and Thomas Greber (University of Zurich). This work was supported by a computer grant at IDRIS-CNRS and LRZ Munich; the work of BW was supported by the European Commission through the Early Stage Researcher Training Network MONET (MEST-CT-2005-020908). MLB thanks the Humboldt Foundation for support through a research fellowship.

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