Fine tuning of graphene-metal adhesion by surface alloying

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We show that bimetallic surface alloying provides a viable route for governing the interaction between graphene and metal through the selective choice of the elemental composition of the surface alloy. This concept is illustrated by an experimental and theoretical characterization of the properties of graphene on a model PtRu surface alloy on Ru(0001), with a concentration of Pt atoms in the first layer between 0 and 50%. The progressive increase of the Pt content determines the gradual detachment of graphene from the substrate, which results from the modification of the carbon orbital hybridization promoted by Pt. Alloying is also found to affect the morphology of graphene, which is strongly corrugated on bare Ru, but becomes flat at a Pt coverage of 50%. The method here proposed can be readily extended to several supports, thus opening the way to the conformal growth of graphene on metals and to a full tunability of the graphene-substrate interaction.

It is well known that the coupling between supported graphene (GR) and the substrate is responsible for a number of properties of GR-based materials, including the electromechanical properties¹, contact resistance², work function³, and ultrastrong adhesion⁴, as well as the electronic⁵⁻¹⁰ and heat transport properties¹¹. Several methods, such as the choice of the substrate¹², the intercalation of adspecies¹³⁻¹⁸, or the creation of an oxide buffer layer¹⁹, have been proven to be a possible means of controlling the graphene-metal interaction, though not ad libitum. These approaches, in fact, do not enable to precisely control the graphene-substrate coupling strength and come with some significant drawbacks. For instance, the penetration of adsorbates between graphene and the substrate requires layer defects to allow intercalation and results in the formation of a non-uniform interface.

We here propose surface alloying as a novel, alternative approach to tailor the GR-substrate interaction to any desired extent. To prove this concept, we grew graphene on a PtRu surface alloy with a variable Pt content. Fig. 1 schematically illustrates our experimental design. Starting from a clean Ru(0001) surface (Fig. 1 (a)), we deposited a variable amount (≤0.5 ML) of Pt on the substrate (Fig. 1 (b)) and annealed the sample to 1300 K in order to promote the intermixing of the two metal species in the top layer (Fig. 1 (c)). As demonstrated by previous studies²⁰, the so obtained PtRu surface alloy exhibits a random distribution of the Pt atoms, which are confined to the first layer. Graphene was subsequently grown by ethylene chemical vapour deposition (CVD) (Fig. 1 (d)), which is a commonly used procedure for the production of large scale graphene. In the present case, a temperature of 1050 K and an ethylene pressure in the range 1 × 10⁻⁷ – 1 × 10⁻⁸ mbar allowed obtaining an extended, well-ordered graphene layer whose interaction with the substrate directly depends on the concentration of Pt atoms.

Results

We first investigated the growth mechanisms and morphology of GR on clean Ru(0001), which represents our reference system. Low Energy Electron Microscopy (LEEM) images acquired during C²H₄ chemical vapour deposition (CVD) at T = 1020 K show that GR grows in a continuous, rolling-carpet fashion (Fig. 2 (a)), in agreement with previous studies²¹,²². The Low Energy Electron Diffraction (LEED) pattern of single-layer GR/Ru(0001) shows the periodicity of a moiré superlattice, formed by (13 × 13) unit cells of GR over (12 × 12) substrate unit cells, in good agreement with the results of higher resolution surface x-ray diffraction images.
experiments. C 1s core level (CL) photoemission measurements performed during CVD (Fig. 2 (b)) show the development of two components, ascribed to populations of strongly (S) and weakly (W) interacting carbon atoms of the graphene layer, both increasing at a linear rate with a constant intensity ratio S:W of ~2.5 (Fig. 2 (c)). The two components are separated by 630 ± 20 meV, in agreement with the value found for an extended GR layer on Ru(0001). Density functional theory (DFT) calculations for GR/Ru(0001) (see Methods), performed with the VASP code, confirm that the GR layer is strongly buckled, with a corrugation of 1.55Å, and a minimum distance from the first Ru layer of 2.15Å. DFT allowed us to calculate the C 1s CL binding energy (BE) for each of the 338 C atoms in the graphene layer.

Figure 1 | Schematic illustration of our experimental design for graphene growth on a PtRu surface alloy. (a) The clean Ru(0001) single crystal. (b) Pt islands (yellow atoms) formed after room temperature deposition of a submonolayer amount of Pt on Ru(0001). (c) The PtRu surface alloy obtained by annealing the system to 1300 K to induce intermixing of the two metal species in the top layer. (d) GR growth on the PtRu surface alloy by ethylene CVD at 1050 K; the C layer starts growing along the substrate steps and subsequently extends to the terraces. (e) Extended, long range ordered GR layer on the PtRu surface alloy.

Figure 2 | Microscopic, spectroscopic and theoretical characterisation of Graphene on Ru(0001). (a) LEEM images of graphene growth on clean Ru(0001) by C2H4 exposure at T = 1020 K (p(C2H4) = 2 × 10⁻³ mbar). In the inset is shown (in grey) the sample area already covered by graphene. (b) C 1s spectra during C2H4 exposure at T = 1020 K. (c) Partial coverage of strongly (S) and weakly (W) interacting GR, and C monomers (CA) as a function of the total C coverage. (d) Side and top view of the DFT-simulated moiré cell of GR/Ru(0001); the colour scale reflects the C-substrate distance. (e) Comparison between the experimental C 1s spectrum of GR and the calculated spectral distribution. The decomposition of the theoretical spectrum into strongly (S-theo) and weakly (W-theo) interacting components is also shown superimposed, along with the histogram of the calculated BE distribution.
atoms of the moiré cell. The experimental spectrum was subsequently fitted to a sum of 338 Doniach-Sunjic functions\(^2\) convoluted with a Gaussian, holding the BEs fixed to the DFT-calculated values. The simulated spectral distribution (Fig. 2 (e)) shows that the two main components actually arise from a continuous distribution of non-equivalent C atomic configurations, thus proving the power of our approach\(^2\) in distinguishing regions of the moiré cells with different degrees of C-substrate interaction. As carbon is deposited on the Ru(0001) surface, another C species (C\(_A\) in Fig. 2 (b)–(c)), which shows up as a small shoulder at 282.82 eV BE, is initially detected before the appearance of GR. This species, which reaches a maximum coverage of \(\sim 0.03\) ML (see inset in Fig. 2 (f)), eventually disappears as GR starts nucleating, with both S and W growing at the expenses of C\(_A\). Notice that we adopt the definition of one monolayer as the coverage yielding one adsorbate for each atom of the substrate surface.

In order to accurately determine the nature of C\(_A\), we calculated the adsorption energies and C 1\(s\) CL BEs of a number of selected C adatoms and dimers adsorbed in non-equivalent configurations, both on the terraces and at the (100) and (111) steps of Ru(0001). We found that the threefold hcp site on the terraces (M\(_{1f}\)) and the C monomer at the steps (M\(_{1d}\)) have very similar adsorption energies (Fig. 3 (a)), thus confirming that, at the typical GR growth temperatures, substrate steps do not act as efficient C monomer trapping centres\(^2\). A comparison between the calculated C 1\(s\) BEs and the experimental spectrum (Fig. 3 (c)), provides direct spectroscopic evidence that the species named C\(_A\) is the C monomer adsorbed at hcp sites on the atomic terraces. As first pointed out by Loginova et al.\(^{21}\), these monomers form a 2D lattice gas which supplies C atoms for GR formation. In the theoretical model of Chen et al.\(^{25}\), GR growth then proceeds through the migration of C monomers to the steps, where dimerization is energetically favoured (\(D\_A - D\_A, D\_B - D\_B\)), and through the subsequent attachment of C atoms.

After this preliminary characterization, we prepared the PtRu surface alloy following a well-established method\(^2\). The so obtained surface alloy is thermally stable above the typical growth temperature of GR, and shows a random distribution of the Pt atoms in the first layer up to a Pt concentration of 80%. The intermixing between the two metals is confined to the first layer of the system, and does not modify the surface lattice parameter with respect to that of clean Ru(0001).

The first difference between Ru(0001) and the PtRu alloy is the GR growth mechanism. At a Pt concentration of 0.5 ± 0.1 ML, LEEM images (Fig. 4 (a)) show that GR first nucleates and grows along the step edges. Only at a later stage, when the number of available sites at the steps has significantly decreased, the GR islands extend to the terraces. The LEED data show that the periodicity of the moiré cell on the PtRu alloy is the same as that of GR/Ru(0001) (see Supplementary Data).

Following the same procedure used for GR/Ru(0001), the evolution of the C 1\(s\) spectra during C\(_2\)H\(_4\) CVD was monitored for various initial Pt concentrations. In this case, the coverage-dependent behaviour of the S and W C 1\(s\) components, is remarkably different from what observed on clean Ru(0001). At low Pt content (0.12 ML, Fig. 4 (b)), the two peaks grow linearly up to a C coverage of \(\sim 2\) ML,
the various C species during C$_2$H$_4$ exposure. The reported S:W intensity ratios were calculated at 2 ML C coverage. A comparison of the simulated spectral distributions (Fig. 5 (c)) clearly shows that the intensity ratio S:W decreases as the Pt concentration in the first layer increases, a trend which faithfully reproduces our experimental observations. Therefore, the larger amount of Pt atoms in the first layer of the alloy leads to a progressive detachment of the C layer from the metal substrate.

Discussion

Although it is widely accepted that graphene interacts weakly with Pt(111) and strongly with Ru(0001)\textsuperscript{12,23}, it is not straightforward to conclude that the presence of Pt in a surface alloy directly weakens the graphene-substrate interaction, and that an increased concentration of randomly distributed guest atoms in the first layer automatically reduces the GR adhesion to the substrate. In fact, the electronic structure of surface and/or near-surface alloys is always largely modified by ligand and strain effects.

The interpretation of our results can be found by using the d-band model which describes the link between adsorption energy and d-band centre\textsuperscript{25}. When the Pt atoms are embedded in a matrix of Ru atoms, the Pt-metal bonds are laterally compressed (2.71 Å) compared to the lattice constant of Pt(111) (2.77 Å). This compression would already induce a weakening of the interaction of any adsorbate with the substrate. In our system, the addition of Pt atoms causes a downshift of the surface projected d-band centre $E_d$ of first-layer atoms with respect to the clean Ru(0001). More specifically, we find that $E_d$ moves from 0.61 eV for bare Ru(0001), to 0.73, 0.84 and 1.20 eV for the surface alloy at Pt coverages of 0.1, 0.2 and 0.5 ML, respectively. These results prove that the d-band model can be extended to describe the trends in the GR-metal interaction, when...
Figure 5 | Density Functional Theory explanation of the variable interaction of graphene grown on the PtRu surface alloy. (a) 2D plot of the simulated moiré cell of GR on the PtRu surface alloy, at various Pt concentrations. The color scale indicates the C-metal distance. The first layer atoms of the substrate are shown superimposed, with the Pt atoms highlighted in a white shade. (b) Simulated difference map (top and side views) of the charge density of graphene on Ru(0001) and PtRu/Ru(0001), with respect to a completely decoupled GR layer on Ru(0001). Red and blue isosurfaces indicate charge accumulation and depletion regions, corresponding to an electron concentration of $\pm 0.023$ e Å$^{-3}$, respectively. Side views: 2D projections of the charge difference map along the plane P normal to the surface plane. (c) DFT-simulated C 1s core level spectra of GR on the Ru and PtRu surfaces, and their deconvolution into strongly (S) and weakly (W) interacting GR components.

the lattice mismatch effects can be separated from the chemical effects. We can therefore expect that graphene on a full monolayer of Pt on Ru(0001) will be even more weakly bonded than a graphene layer on Pt(111).

The interplay between lattice mismatch and chemical effects has already been addressed in the case of strongly interacting graphene-substrate systems (as in the case of Ni(111) and Fe(110)$^{31}$), for which the lattice mismatch has been shown to play a secondary role. Our experiments, on the other hand, prove that a similar trend applies also to the case of weakly interacting systems. More specifically, starting from a strongly coupled system like GR/Ru(0001) and gradually changing the chemical composition of the substrate while keeping the lattice constant unchanged (as for PtRu and Ru(0001)), the graphene interaction is significantly modified. Our findings hence provide direct evidence that the interaction strength is dominated by chemical effects rather than by the geometrical lattice mismatch between graphene and the substrate.

In conclusion, we have proven that a bimetallic surface alloy can be used to grow an extended and thermally stable high-quality graphene layer, whose interaction with the support can be selectively tuned by modifying the chemical composition of the first layer of the substrate. The modulation in the GR-substrate coupling can be described in terms of the d-band model.

The understanding of the physical mechanisms responsible for the different levels of adhesive interaction could be of impact to the fabrication and performance of devices based on graphene-metal junctions, and to the integration of graphene in hybrid two-dimensional structures. It will also potentially find use in surface protective coatings and high-power nanoelectronic applications for which a low thermal and electrical resistance are a fundamental requirement, along with a high thermal stability$^{32}$.

Methods

Experimental methods. The photoemission experiments were performed at the SuperESCA beamline of the third-generation synchrotron radiation source Elettra in Trieste. The ultrahigh vacuum chamber (base pressure $\leq 2 \times 10^{-10}$ mbar) is equipped with standard surface science facilities for sample cleaning and characterization, and with a Phoibos hemispherical electron energy analyser from SPECS (mean radius of 150 mm), combined with a custom home-made delay-line detection system. The energy tunability and the high brilliance of synchrotron radiation allow monitoring in real-time the evolution of the atomic core levels of the sample under reaction conditions. The overall experimental resolution attained in our experiments was of the order of 50 meV for the C 1s signal.

Low energy electron microscopy (LEEM) is a well-established technique used for imaging dynamic processes at surfaces and interfaces. It employs slow electrons to probe crystalline specimens, using backscattered electron for imaging surfaces. It can be used in bright- or dark-field mode, depending on whether primary or secondary diffracted beams are employed. The LEEM experiments presented in this work were carried out at the Nanospectroscopy beamline of the Elettra synchrotron radiation facility using the SPELEEM III microscope (Elmitec). This instrument combines low energy electron microscopy and diffraction with energy filtered X-ray photoemission microscopy. The current lateral resolution is close to 10 nm in LEEM mode. The diffraction measurements are restricted to an area of about 2 μm in diameter.

The Ru(0001) crystal was cleaned by repeated cycles of Ar$^+$ sputtering at 2.5 keV (p(Ar) = 3 × 10$^{-7}$ mbar) and annealing to 1500 K, followed by a high temperature oxidizing treatment to remove bulk C contaminants (p(O$\,$2) = 5 × 10$^{-7}$ mbar; 550 < T < 1100 K), and a reducing treatment in H$_2$ atmosphere to remove residual oxygen (p(H$_2$) = 2 × 10$^{-7}$ mbar; 550 < T < 1500 K). The C 1s, O 1s and S 2p CL spectra after this procedure show no evidence of residual contaminants. The PtRu surface alloy was prepared following the method developed by Diemand et al.$^{33}$.

A submonolayer amount of Pt was first deposited at room temperature on clean Ru(0001) using a Pt evaporator. Annealing the as deposited layer to 800 K results in the formation of Pt ad-islands covering the Ru(0001) surface, which appear as bright spots in the LEEM images. The grey scale contrast between the bright Pt-covered areas and the homogeneous Ru(0001) substrate in the background was exploited to estimate the amount of Pt deposited on the sample prior to alloying, using a particle analysis algorithm. More specifically, the border of the bright islands was first detected by differentiating the images in the x and y dimensions (the maximum gradient corresponding to edge regions), and the regions defined by the edges were then measured and compared with the total area of the image. In order to promote the
formation of a random alloy in the Ru(001) surfaces with Pt atoms embedded in the first layer of Ru, we annealed the surface to 1300 K. The Pt islands visible after Pt deposition (see LEEM image in Supplementary Fig. S1 (a)) irreversibly disappear upon annealing (see Supplementary Fig. S1 online (b)). The surface at this stage shows a uniform contrast in LEEM, thus signifying a redistribution of the Pt atoms in the Ru surfaces, as previously demonstrated by extended STM experiments performed by the group of Behm [24].

In the photoemission experiments, the Pt coverage was estimated by comparing the intensities of the Pt 4f peaks, and of the Ru 3d peaks, after normalizing them to the photon flux and to the photoelectron cross section. The Ru 3d peaks photoemission intensity, which receives a contribution from both bulk and surface Ru atoms, was additionally revealed as to account for the depth-dependent signal attenuation due to the inelastic electron photoemission mean free path in the crystal, as derived from the Tanuma, Powell, and Penn formula [25]. The Pt 4f peaks core level spectrum, acquired after Pt evaporation on the clean Ru(0001) substrate, both before and after annealing to 1300 K can be fitted to a single component ascribed to the surface alloy, which does not appreciably lose intensity upon annealing, thus ruling out Pt bulk dissolution at Pt coverages ≤0.5 ML.

**Theoretical methods.** The density functional theory (DFT) calculations have been performed with the VASP code [26], using PAW potentials [27] and the PBE exchange-correlation functional [28]. Single particle orbitals were expanded in plane waves (PW), with a planewave kinetic energy cutoff of 400 eV. The lattice parameter of Ru was used to model both the Ru(001) surface and the PtRu/Ru(001) surface alloy. The adsorption of graphene on the Ru(001) surface has been modelled by overlaying a (13 × 13) graphene sheet over a (12 × 12) Ru(001) super-cell and using a slab of 5 layers. In all the calculations the energy was minimized until the forces acting on the atoms were smaller than 0.01 eV/Å. A vacuum interspace of at least 10 Å was used to minimize the interaction between periodic images of the slab along the direction perpendicular to the surface, resulting in a supercell of 21.5 Å along the z axis. The SCs were calculated in the final state approximation as described in Ref. 25.38 We used the Γ point only to sample the Brillouin zone. Spot checks using a 2 × 2 × 1 grid showed that with the Γ point SCs are converged to better than 5 meV. For the clean surface, we used up to 7 atomic layers, and the results show that with 5 or more layers the SCs are converged to within ~10 meV. Charge density differences have been calculated as \( n_{\text{GR}} - n_{\text{Ru}} = n_{\text{GR}} - n_{\text{Ru}} \), where \( n_{\text{GR}} \) is the total electronic charge density of the clean graphene slab and \( n_{\text{Ru}} \) is the charge density of the isolated slab with exactly the same geometry and \( n_{\text{GR}} \) the charge of the GR layer, also in the same geometry as when adsorbed on the slab.

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