

# Probing growth dynamics of graphene/Ru(0001) and the effects of air exposure by means of helium atom scattering



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## ABSTRACT

The growth dynamics of graphene on Ru (0001) and the air stability of this interface have been studied by helium atom scattering. Graphene on Ru (0001) shows high reflectivity for impinging atomic (He) and molecular (H<sub>2</sub>) beams. The diffraction pattern shows the occurrence of peaks arising from the Moiré pattern. Air exposure reduces He-atom reflectivity, due to water dissociation at the graphene/metal interface and the subsequent formation of C–H groups. However, upon annealing at 450 K the reflectivity of pristine graphene has been recovered. The exposure to atomic hydrogen induces a reduction of the reflectivity by more than the 65% with respect to the initial value.

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## 1. Introduction

The growth of graphene on metal substrates continues to attract great interest [1–4] for both technological and fundamental interest. In fact, graphene–metal contacts are unavoidable and omnipresent components in graphene-based devices [5–8]. Moreover, the comprehension of the existing hybridization between graphene  $\pi$  states and metal d bands has intrinsically high fundamental interest [1,9,10].

The preparation of highly-ordered graphene could be extended up to the millimeter scale for epitaxial graphene grown on Ru(0001) [11]. No bond breakage has been revealed even over the substrate steps.

The lattice mismatch (9%) between C and Ru causes the formation of an incommensurate or reconstructed interface [12–14]. Scanning tunneling microscopy (STM) measurements display a periodically rippled hexagonal pattern with a lattice constant of 30 Å (about 12 graphene unit cells) overlaid on 11 Ru(0001) unit cells [15–17]. The periodicity of the ripples is determined by the difference in lattice parameter of graphene and substrate. The apparent height modulation has been found to vary, depending on tip conditions and tunneling parameters, between 0.6 and 1.5 Å [16]. A density-functional theory (DFT) study by Wang [31] found a corrugation of 1.5 Å, while DFT calculations reported in Ref. [18] showed that the interfacial corrugation is weak and the graphene layer has a corrugation of only 0.4 Å. The apparent discrepancy is due to the interplay between electronic and geometric effects in the measured corrugation [19]. In particular, in STM imaging the electronic contribution prevails over the topographic one [20].

The height and width of these ripples are consistent with models allowing the carbon ions to form different types of bonds. In particular, carbon atoms located at the higher areas of the superstructure are on three-fold hollow sites and they scarcely interact with the substrate. On the contrary, some of the carbon atoms closer to the Ru substrate occupy atop positions and show a strong chemical bonding with the substrate. A strong hybridization between 2p<sub>z</sub> states of carbon atoms and the 4d<sub>z<sup>2</sup></sub> orbitals of Ru occurs [21]. Charge is accumulated on the C atoms in atop positions and depleted at the Ru atoms [22]. It has been demonstrated [21] that the preferential direct C–Ru bond at atop sites results in a distribution of compressive and tensile strains in the adlayer so as to cause the corrugation of graphene. Hence, the strong covalent bonding between graphene and Ru (0001) is correlated to the degree of graphene corrugation [21,23].

The existence of this curved region in the graphene sheet can thus have strong effects on the physical and chemical properties.

Helium atom scattering (HAS) is a powerful tool for monitoring the dynamics of the formation of the overlayer and its reactivity. Measuring the growth dynamics provides a unique opportunity to study atomic-scale interactions [24]. With respect to growth studies, a major advantage of HAS as compared with other techniques is its high sensitivity to step distributions in the topmost surface layer [24], which allows a quite simple interpretation of the data.

Herein, we report on growth dynamics of graphene/Ru(0001) and its modification by air exposure.

## 2. Experimental

The Ru(0001) substrate has been prepared in an ultra-high vacuum (UHV) chamber with a base pressure in the range of 10<sup>−8</sup> Pa. The chamber is equipped with a reverse view low-energy electron diffraction

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(LEED) optics that allow us to do Auger spectroscopy, and facilities for ion sputtering, evaporation and gas exposure. The Ru(0001) crystal has been cleaned by cycles of Ar<sup>+</sup> sputtering followed by oxygen exposure at 1200 K and successive heating to 1600 K.

The He diffraction apparatus consists of a three-stage differentially pumped beam system and an 18 in. diameter UHV scattering chamber. The free jet expansion is produced through a nozzle of  $d = 10 \mu\text{m}$  diameter. Measurements reported here were performed with a source pressure  $P_0 = 70$  bar behind the nozzle and with a nozzle temperature of 300 K. The velocity spread of the He beams was estimated to be 3% under these conditions. The base pressure in the chamber was typically  $2 \times 10^{-8}$  Pa, reaching  $4 \times 10^{-8}$  Pa with the He beams on. The angular distribution of the scattered molecules has been analyzed with a quadrupole mass spectrometer mounted on a two-axis goniometer. This arrangement allows rotations of  $200^\circ$  in the scattering plane (defined by the beam direction and the normal to the surface) as well as  $\pm 15^\circ$  from the scattering plane for a fixed angle of incidence.

Vibrational and plasmon investigations have been carried out at the University of Calabria, Department of Physics with a Delta 0.5 spectrometer (SPECS GmbH, Germany) for high-resolution electron energy loss spectroscopy (HREELS) with an energy resolution of 4 meV.

Around each spot of the  $(1 \times 1)$  LEED pattern, satellite spots due to the  $(12 \times 12)$  reconstruction of the overlayer have been revealed, as a consequence of the existence of ripples [19,25] (Fig. 1).

### 3. Results and discussion

The dynamics of the formation of the graphene layer has been followed by monitoring the intensity of the (00) diffraction peak of the atomic He beam in time in an ethylene environment (Fig. 2). To prepare graphene, the Ru(0001) crystal has been exposed to ethylene at 1150 K in UHV. A single layer of graphene has been deposited by dosing ethylene at a pressure of  $3 \times 10^{-6}$  Pa for 600 s (24 L, region A of Fig. 2).

The analysis of the reflectivity in region A (during the above-mentioned growth procedure) indicates the saturation of the monolayer graphene (MLG), so that the entire surface is covered by the same periodic superstructure. In correspondence of such surface, well-defined phonon modes have been revealed, as shown elsewhere [26]. The growth of graphene on Ru(0001) via C<sub>2</sub>H<sub>4</sub> adsorption and dissociation has been recently characterized in details [27]. Ethylene dissociates to ethylidyne species [28], which partly dehydrogenate to form acetylide. Above room temperature, the acetylide formation is favored. Between 500 and 700 K the complete dissociation of hydrocarbons occurs. Carbon clusters on the surface coalesce forming monolayer graphene for temperatures higher than 700 K. For annealing temperatures above 1000 K, carbon atoms aggregate to steps, thus increasing the size of monolayer graphene islands.

Upon exposure of C<sub>2</sub>H<sub>4</sub> the overall reflectivity of the specular peak ( $I_{00}$ ) decreased by about the 79% (region A). After a cooling down to

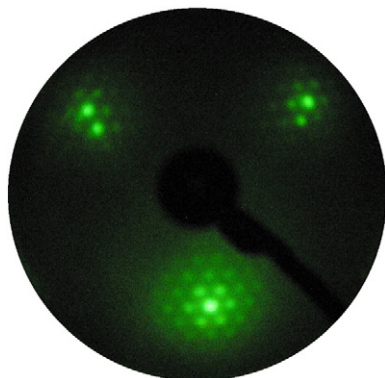


Fig. 1. LEED pattern of graphene on Ru (0001), recorded at  $E_p = 74$  eV and at room temperature. Spots are due to the moiré reconstruction of the graphene sheet.

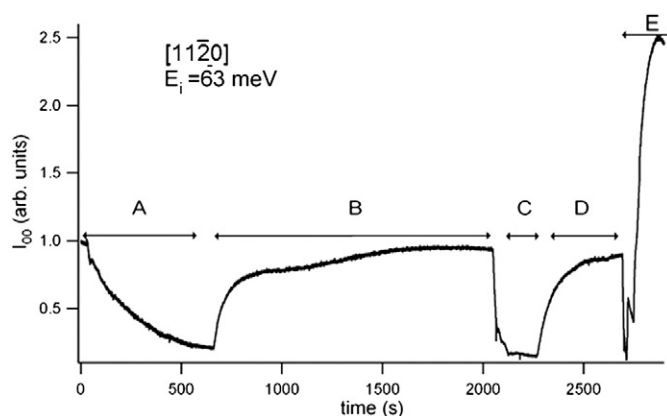


Fig. 2. Intensity of the specular peak  $I_{00}$  as a function of time in an ethylene environment with partial pressure  $3 \times 10^{-8}$  mbar. Region A is related to C<sub>2</sub>H<sub>4</sub> adsorption and its dissociation (graphene formation), while Region B refers to the cooling down to 100 K. The sample was further annealed at 1150 K (Region C) and cooled to 100 K (Region D). The significant increase of the reflectivity upon annealing at 1600 K (Region E) suggests that graphene desorption starts at 1400 K.

100 K (region B) the amplitude of the  $I_{00}$  peak increased due to the thermal attenuation of the coherent diffraction intensities [43]. A similar behavior has been obtained upon a second annealing at 1150 K (region C) and a successive cooling at 100 K (region D). However, the reflectivity increased of the 250% by annealing at 1600 K (region E). For sample heating at temperatures higher than 1400 K, carbon atoms desorb from the surface. This is also confirmed by the increased reactivity of the adlayer annealed at 1600 K that resembles that of the bare substrate and by the disappearance of the LEED pattern of the adlayer.

Fig. 3 shows the in-plane ( $\Phi = 0^\circ$ ) and out-of-plane ( $\Phi = 1.3^\circ, 15.5^\circ$ ) diffracted peaks detected when scattering a beam of He of 43 meV off MLG grown on Ru (0001). The intensity of the specularly reflected (00) peak depends on the crystalline quality of graphene, reaching 25% of the incident beam for highly ordered samples. The in-plane He-diffraction spectrum shows both the  $(1/12, 1/12)$  first peaks of the Moiré superstructure of bumps and the  $(-1, -1)$  of the C lattice. Notice that the appearance of the first Moiré peaks and the  $(-1, -1)$  in the same in-plane scan can not be taken as an indication that the corresponding lattices are aligned.

For molecular beams of hydrogen, a reflectivity of the 12% has been reached.

The He-atom beam reflectivity of MLG decreases upon air exposition (Fig. 4). The sample has been exposed to air and transferred to the UHV chamber without any cleaning procedure except a flash annealing at 450 K. The reflectivity of the as-deposited sample has fully recovered upon annealing (Fig. 4). However, the decrease of the He reflectivity points out to a non perfect inertness of the graphene/metal interfaces.

To shed the light on the chemical reactivity of air-exposed graphene/metal interfaces, we have carried out a complementary vibrational study at room temperature. Vibrational spectroscopy is a powerful tool for identifying chemisorbed species at surfaces and, moreover, the species generated by surface reactions [29]. In particular, high-resolution electron energy loss spectroscopy (HREELS) is particularly suitable for such aims for its surface sensitivity and its high energy resolution [30].

In Fig. 5 we compare HREELS spectra acquired for MLG/Ru(0001); after that the graphene sample was exposed to air (top spectrum) and to 2500 L of H<sub>2</sub>O in vacuum conditions (bottom spectrum) at room temperature. Bands at 334 and 365 meV in the air-exposed sample and at 334 meV in the water-exposed graphene in UHV conditions indicate that water dissociation occurs in both cases. In fact, such bands unambiguously arise from stretching vibrations of C–H [31].

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