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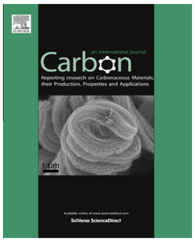

Modulating charge density and inelastic optical response in graphene by atmospheric pressure localized intercalation through wrinkles

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ABSTRACT

The intercalation of an oxide barrier between graphene and its metallic substrate for chemical vapor deposition is a contamination-free alternative to the transfer of graphene to dielectric supports, usually needed for the realization of electronic devices. Low-cost processes, especially at atmospheric pressure, are desirable but whether they are achievable remains an open question. Combining complementary microscopic analysis, providing structural, electronic, vibrational, and chemical information, we demonstrate the spontaneous reactive intercalation of 1.5 nm-thick oxide ribbons between graphene and an iridium substrate, at atmospheric pressure and room temperature. We discover that oxygen-containing molecules needed for forming the ribbons are supplied through the graphene wrinkles, which act as tunnels for the efficient diffusion of molecules entering their free end. The intercalated oxide ribbons are found to modify the graphene–support interaction, leading to the formation of quasi-free-standing high quality graphene whose charge density is modulated in few 10–100 nm-wide ribbons by a few 10^{12} cm^{-2}, where the inelastic optical response is changed, due to a softening of vibrational modes – shifts of Raman G and 2D bands by 6 and 10 cm^{-1}, respectively.

1. Introduction

Owing to its two-dimensional topography, graphene, an atomically-thin sheet of carbon atoms arranged in a honeycomb lattice, is optimally accessible for local tuning of its properties. In this respect, patterning and local doping of graphene have received considerable attention. The first route, recently demonstrated by growth onto a patterned substrate, allowed to achieve a long-standing goal, that of opening substantial band gaps close to the Fermi level in graphene [1]. The second route has been thus far pursued with the help of local gates engineered with nanofabrication techniques, either deposited on top [2–4] or placed below [5] graphene, and opened the exploration of ballistic electron optics effects with massless Dirac fermion-like electrons, such as Klein tunneling [6,2,3]. Combining both patterning and local doping made it possible to build controllable graphene-based optical absorbers [7]. Further exploiting graphene's potential as a metamaterial, for instance for confining optical plasmons [8] or for guiding ballistic electrons in graphene [9], pushes the development of methods yielding graphene with modulated charge density.

Various processing steps in these methods however usually induce spurious changes of charge density and other

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properties. The transfer of graphene prepared by chemical vapor deposition (CVD), onto a suitable support, for instance causes ill-controlled p-doping of graphene [10], and the deposition of top electrodes for controlling the charge density usually generates diffusive graphene regions (see Refs. [3,4] and references therein). Alternative methods, avoiding these polluting steps, are thus desirable. Intercalation of species between a metallic substrate needed for CVD and graphene, a method known since the 1980s [11], is an efficient one as we show in this article. It is a versatile way to achieve quasi free-standing graphene [12] and to engineer the properties of graphene, for instance to induce electronic band-gaps [13], magnetic moments [14], and strains [15]. Dual intercalation, of silicon and oxygen, even showed great promise for the transfer-free preparation of graphene-on-oxide field effect transistors [16].

Despite the numerous reports devoted to graphene/substrate intercalated systems however, two key questions remain open. First, the surmised role of defects as pathways for intercalation has only been established, yet partially in some cases, for a few defects, namely graphene free edges [12] and point defects [17,18]. Unveiling other intercalation pathways will help better envisioning the full potentialities of intercalation for building up advanced graphene-based hybrids. Second, all studies of intercalation reported thus far were performed under ultra-high vacuum (UHV). While this approach offers optimum control over the processes, it is a prohibitively costly one in the view of the production of graphene decoupled from its substrate. Atmospheric pressure intercalation would be desirable, but it may proceed differently from UHV intercalation, due to the markedly different conditions.

In this article we address these two questions, by studying high quality graphene prepared by CVD on Ir(111) thin films. Iridium is one of those transition metals, like Cu, Pt, and Au, that weakly interact with graphene [19]. Unlike on the latter three metals however, most defects and notably grain boundaries can be avoided on Ir(111) [20,21], so that their role in intercalation [17] can be ruled out. Correlating complementary microscopic analysis, atomic force microscopy (AFM), scanning tunneling microscopy (STM) and spectroscopy, local work-function (WF) analysis and X-ray photoelectron spectroscopy in a photoemission electron microscope (PEEM), and local Raman spectroscopy, we show that exposure to air at room temperature leads to the formation of an ultrathin intercalated oxide modifying the weak graphene–Ir interaction and generating local variations of the charge density in graphene. We find that a common kind of defect, local delaminations of graphene from its substrate, so-called wrinkles, forming during cool down to room temperature after CVD due to the mismatch of thermal expansion coefficient of graphene and its substrate, are pathways for a slow intercalation of oxygen species.

2. Experimental

Graphene was prepared by CVD at 1300 K with ethylene, in a UHV system with 10^{-10} mbar base pressure, on Ir(111) thin films previously deposited on C-plane sapphire wafers [22]. Before exposure to air, the sample surface was imaged by *in situ* room temperature STM. The growth was stopped after few minutes of exposure to a 10^{-8} mbar partial pressure of ethylene in order to achieve a partial coverage of graphene.

AFM was performed in tapping mode in atmospheric pressure. Raman scattering measurements were done in atmospheric pressure with a WITec spectrometer (600 lines/mm grating) coupled to an excitation laser with 532 nm wavelength and 2 mW/cm^2 power, and a 100× objective lens allowing a spatial resolution of about 300 nm. Each Raman spectra on the maps are measured with a 5 s acquisition time. PEEM measurements were done under UHV after mild degassing (500 K) of the sample for 1 h, using a NanoESCA spectromicroscope (Omicron NanoTechnology). For the WF analysis, a UV Hg light source (4.9 eV) was used; the lateral resolution was better than 150 nm and the typical sensitivity of the WF determination was 20 meV. For the photoemission micro-spectra, a focused X-ray source (1486 eV) was illuminating the typical 35 μm field of view, and area selection over 5 μm-wide regions was performed thanks to a field aperture located in the first intermediate image plane of the PEEM optics; the overall energy resolution was 0.8 eV. *Ex situ* STM measurements were performed in a variable temperature STM. The spectra displayed are the average over 132 spectra, each obtained over 132 different points separated by 3.1 nm in each of the regions. *Ex situ* STM images were acquired with 100 pA and 800 mV tunneling current and bias, respectively.

3. Results and discussion

Under UHV, prior to exposure to air the graphene-covered regions of the sample exhibit a typical flat topography, except for wrinkles and a periodic corrugation associated with the graphene/Ir(111) moiré [23] (Fig. S1 in the Supplementary material). The situation is markedly different after room temperature exposure to air, as shown by AFM. Inspecting phase contrast AFM images (Fig. S2 in the Supplementary material) allows one to identify graphene-free and graphene-covered regions [24]. Fig. 1a reveals that (i) graphene-free regions (named A hereafter) protrude out of the surface, (ii) around graphene edges and along wrinkles, flat ribbons (named B hereafter) whose height is substantially larger (see below) than the Ir atomic step edges, are found. The moiré observed with STM under UHV before air exposure is no more visible [25].

While the height (typically 3 nm in average, relative to graphene) of type A-regions does not evolve with time, the height of type B-regions, as well as their lateral expansion, does (Fig. 1b and c). From 0.4 nm and several 10 nm after 1 h of exposure to air, the height and width of type B-regions increases, first rapidly, then slower and slower. After a few days they do not increase much and reach about 1.5 nm and a few 100 nm, respectively. The increase can be stopped at any stage by simply placing the sample under UHV. The surface of graphene appears rougher on type-B regions than on other graphene regions, as seen in STM images (Fig. 2). What is the nature of the height variations upon exposure to air? Volume expansion of surfaces due to their oxidation is a well-known effect in AFM [26]. The presence of type A-regions is inter-