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Hydrogen intercalation under graphene on Ir(111)

Elin Grånäs [a,1], Timm Gerber [b], Ulrike A. Schröder [b], Karina Schulte [c], Jesper N. Andersen [a,c], Thomas Michely [b], Jan Knudsen [a,c,*]

[a] *Division of Synchrotron Radiation Research, Department of Physics, Lund University, Box 118, 221 00 Lund, Sweden*
[b] *II. Physikalisches Institut, Universität zu Köln, 50937Köln, Germany*
[c] *MAX IV Laboratory, Lund University, Box 118, 221 00 Lund, Sweden*

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ABSTRACT

Using high resolution X-ray photoelectron spectroscopy and scanning tunneling microscopy we study the intercalation of hydrogen under graphene/Ir(111). The hydrogen intercalated graphene is characterized by a component in C 1*s* that is shifted −0.10 to −0.18 eV with respect to pristine graphene and a component in Ir 4*f* at 60.54 eV. The position of this Ir 4*f* component is identical to that of the Ir(111) surface layer with hydrogen atoms adsorbed, indicating that the atomic hydrogen adsorption site on bare Ir(111) and beneath graphene is the same. Based on co-existence of fully- and non-intercalated graphene, and the inability to intercalate a closed graphene film covering the entire Ir(111) surface, we conclude that hydrogen dissociatively adsorbs at bare Ir(111) patches, and subsequently diffuses rapidly under graphene. A likely entry point for the intercalating hydrogen atoms is identified to be where graphene crosses an underlying Ir(111) step.

1. Introduction

Understanding and controlling intercalation of molecules between epitaxial graphene and its substrate is important for processes such as: exfoliation, doping of graphene from the backside [1], manipulation of the adsorption behaviors from the backside of graphene [2–4], under-cover catalysis beneath the graphene layer [5,6], and functionalizing of graphene [4].

The majority of the studies that address hydrogen adsorption on Ir(111) supported graphene used the dosing of atomic hydrogen to decorate graphene with hydrogen atoms from the frontside [7–9]. The main conclusion from these studies is that H atoms preferentially adsorbs in the areas of the graphene moiré, where locally every second C atom is sitting atop of an Ir substrate atom enabling hydrogen chemisorption-induced sp^3 rehybridization of graphene. This rehybridization is signaled mainly as positive core level shifts (CLSs) in the C 1*s* signal of graphene.

Surprisingly enough, and in contrast to the quite detailed knowledge about hydrogenation of graphene using atomic hydrogen, very little is known about hydrogen intercalation under graphene resting on its noble metal surface. The only exception is the work by Balgar et al. [4], who proposed graphane formation after room temperature exposure to molecular hydrogen followed by subsequent exposure to atomic deuterium. Here we present for the first time a reproducible recipe for hydrogen intercalation using molecular hydrogen and give direct evidence of a single phase of intercalated hydrogen beneath graphene. We give a complete picture of hydrogen intercalation, provide X-ray photoelectron spectroscopy fingerprint data, show the impossibility to intercalate a complete graphene layer using molecular hydrogen, demonstrate that bare Ir(111) patches are needed to achieve intercalation of a partial graphene layer, and eventually identify the entry point for hydrogen atoms to diffuse under graphene flakes.

2. Experimental details

The high resolution X-ray photoelectron spectroscopy (HRXPS) experiments were carried out at beamline I311 [10] at the MAX IV Laboratory in Lund, Sweden, with a base pressure in the experimental chamber below $1 \cdot 10^{-10}$ mbar. All XP-spectra were collected in normal emission with photon energies of 120 eV for Ir 4*f*, and 390 eV for C 1*s*. The total energy resolution of the light and analyzer is better than 45 meV and 60 meV for the respective core level spectra. All spectra were fitted with Doniach–Šunjić functions convoluted with Gaussians, with a linear background.

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[*] Corresponding author.
E-mail address: jan.knudsen@sljus.lu.se (J. Knudsen).

[1] Present address: DESY Nanolab, Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22603 Hamburg, Germany.

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STM measurements were carried out at a variable temperature scanning tunneling microscopy (STM) system in Cologne with a base pressure below $1 \cdot 10^{-10}$ mbar. STM topographs were post processed using the WSxM software [11].

In both laboratories, the Ir(111) crystal was cleaned by cycles of noble gas ion sputtering at room temperature, annealing in oxygen ($1 \cdot 10^{-7}$ mbar, 5 min) at 1200 K, and vacuum annealing to 1350 K. The cleanness of the crystal was confirmed with XPS or STM. Temperatures were measured with chromel–alumel thermocouples attached directly to the crystal.

Sub-monolayer graphene coverages of 0.2 ± 0.05 ML or 0.5 ± 0.1 ML were grown by one or three cycles of ethylene (C_2H_4) adsorption to saturation at room temperature followed by thermal decomposition at 1350 K [12]. 0.2 ML graphene consists of islands with typical diameter of the order of 30 m. The 0.5 ML graphene layer is not yet percolated and consists of islands and coalesced islands with typical diameter of the order of 50 nm [3]. A full 1 ML graphene film was grown by one cycle of ethylene adsorption and thermal decomposition at 1350 K followed by chemical vapor deposition of ethylene ($1 \cdot 10^{-7}$ mbar) for 30 min at 1270 K. The full coverage of the 1 ML graphene was confirmed by exposing the film to 750 L of O_2 ($1 \cdot 10^{-5}$ mbar, 100 s) at 575 K. From our previous studies we know that sub-monolayer graphene would become intercalated by oxygen at these conditions [3]. On the 1ML graphene grown with the above procedure none of the characteristics of oxygen intercalated graphene was observed: both the C 1*s* and Ir 4*f* regions were identical to before oxygen dosing and no oxygen signal was observed in O 1*s* (spectra not shown).

Graphene grown by these procedures forms an incommensurate moiré unit cell consisting of (10.32 × 10.32) graphene unit cells on (9.32 × 9.32) Ir unit cells, with the dense packed rows of graphene and Ir(111) in parallel and with an orientation scatter of less than ± 0.5° [13]. Low energy electron diffraction (LEED) confirms the excellent quality of our graphene and the absence of rotational variants [14].

Among the different preparation recipes, we identified the following to give the cleanest intercalated H-structure under graphene, with an minimum of contamination caused by adsorption from the residual gas: After graphene growth the sample was (i) cooled to 140 K with liquid nitrogen, (ii) flashed to 620 K to desorb molecules that adsorbed from the residual gas during the cooling of the manipulator and sample, (iii) cooled quickly to 140 K, and (iv) exposed to molecular hydrogen below this temperature with a pressure of $5 \cdot 10^{-6}$ mbar for 200 s (750 L). A dose of 750 L at 140 K is sufficient to achieve an H-coverage close to saturation on Ir(111) [15]. (v) During transfer between the preparation and the XPS analysis chamber a background molecular hydrogen pressure of $1 \cdot 10^{-7}$ mbar was used to prevent desorption of hydrogen atoms and adsorption of CO from the residual gas. This method of intercalation is used if not stated otherwise in the text.

3. Results and discussion

In Fig. 1 the C 1*s* spectra of 1 ML and 0.2 ML graphene on Ir(111) before (lower spectra) and after (upper spectra) exposure to 750 L molecular hydrogen at 130–140 K are displayed. Initially, both the 1 ML and 0.2 ML graphene peak can be fitted by a single component, C_{Ir} (284.09 ± 0.01 eV). Its position is in agreement with our earlier studies of graphene on Ir(111) [3,16] After exposure to 750 L molecular hydrogen at 140 K the C 1*s* peak of 1ML graphene remains unaffected, as Fig. 1 (a) clearly demonstrates. In contrast, the C 1*s* peak of the 0.2 ML graphene film becomes wider towards the low binding energy side, and it is now best fitted by two components: one new component, C_H, shifted −0.10 eV having 20 % of the total intensity, and one C_{Ir} component identical to pristine graphene having 80% of the total intensity. Atomic hydrogen adsorbed on graphene/Ir(111) mainly give rise to C 1*s* core level shifts (CLS) between +0.5 eV and +0.9 eV assigned to sp^3 hybridized graphene and graphene bound to hydrogen dimers [7,9]. Thus the CLS of −0.10 eV observed for the C_H component shows that exposure to molecular hydrogen onto 0.2 ML graphene gives rise to formation of a very different species, compared to the ones arising from exposure to atomic hydrogen. Therefore, we assign the new C_H component to hydrogen intercalated graphene. The fact that the C_H component has only a weight of 20 % implies a correspondingly small fraction of the graphene area to be intercalated. Furthermore, as the C 1*s* peak of 1 ML graphene is entirely unaffected by the molecular hydrogen dosing we conclude that molecular hydrogen is unable to intercalate a full monolayer film. Bare Ir(111) patches must therefore be essential for hydrogen intercalation.

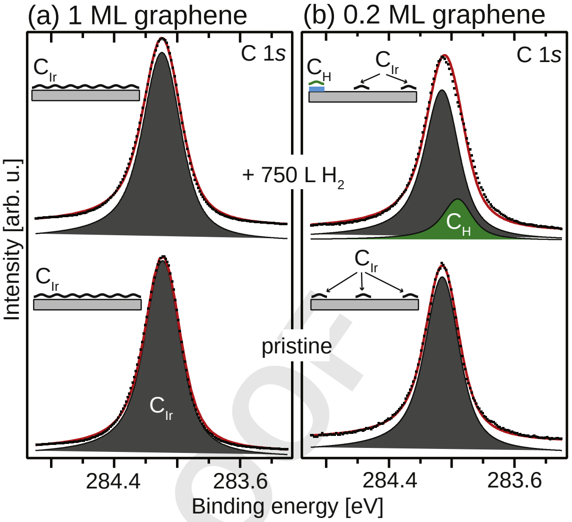

Fig. 1. C 1*s* region of (a) 1 ML and (b) 0.2 ML graphene before (lower spectra) and after (upper spectra) exposure to 750 L at 140 K (1 ML) or 130 K (0.2 ML). The measured spectra are shown as black dots, the fitted spectra as red lines and the fitted components as filled peaks. The dark gray peak corresponds to the pristine graphene component, C_{Ir}, and the green to the hydrogen intercalated component, C_H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2 (a), (b), and (c) shows the Ir $4f_{7/2}$ regions of 1 ML graphene, 0.2 ML graphene, and 0 ML graphene before (lower spectra) and after (upper spectra) exposure to 750 L molecular hydrogen at 130–140 K. Before exposure all spectra can be fitted by two components, Ir_B corresponding to Ir bulk atoms and Ir_S corresponding to Ir surface atoms both with and without graphene above. The peaks are located at 60.82 ± 0.01 eV and 60.31 ± 0.01 eV, respectively. The surface component of Ir has previously been seen to be sensitive to adsorption of molecular hydrogen [17] and inspection of panel (a) clearly demonstrates that for 1 ML the Ir $4f_{7/2}$ spectra is unaffected by molecular hydrogen dosing. This underlines our conclusion that molecular hydrogen is unable to intercalate 1 ML graphene.

In contrast, for 0.2 ML graphene the intensity of the Ir_S component decreases and a new component, Ir_H (78 %), appears at 60.54 ± 0.04 eV upon exposure to molecular hydrogen [see upper spectrum in (b)]. A very similar Ir_H component is observed on Ir(111) without any graphene after an identical molecular hydrogen exposure. On Ir(111), molecular hydrogen exposure is known to adsorb dissociatively, with the hydrogen atoms sitting in on top position in a p(1× 1)-H structure [15,18,19]. We therefore assign the Ir_H component to Ir surface atoms and Ir atoms at the graphene interface bound to hydrogen atoms atop.

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