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Synthesis of epitaxial graphene on rhodium from 3-pentanone

Silvan Roth*, Jürg Osterwalder, Thomas Greber

Physik-Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

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ABSTRACT

The synthesis of high quality single layer graphene on rhodium, *g*/Rh(111), is reported. The graphene layers are grown at 1060 K by low pressure chemical vapor deposition (CVD) using 3-pentanone as a precursor molecule. The presented growth technique shows an easy high quality production method for epitaxial graphene monolayers. The chemical composition and structural properties of such self-assembled monolayers were characterized by X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). Scanning Tunneling Microscopy (STM) confirms the formation of a 3 nm super cell and a unique surface morphology which establishes the potential of *g*/Rh(111) as a template for molecules.

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1. Introduction

The application of graphene in future electronic devices [1] or its use as a template for molecular self assembly [2] demands high quality production methods of this material of the day. Growing graphene by chemical vapor deposition on various substrates is a booming field of research, since it is a possible route towards mass production of such layers [3]. The growth of graphene on Rh(111) has been demonstrated [4–7] as well as on other metal substrates such as Ni [8], Cu [3,5], Ir [9], or Ru [10–12]. On substrates with carbon in the bulk such as Ru [10,13] or SiC [14] graphene can be formed by segregation from the bulk. For the growth of graphene on rhodium, various precursors have been used. Müller et al. exposed a clean rhodium surface ex-situ to liquid acetaldehyde $H_3-C(OH)$ or acetone $CH_3-C(O)-CH_3$ and then annealed the sample in ultra high vacuum to 1000 K which leads to a single layer graphene [4]. An all in situ preparation was realized by ethene C_2H_4 at a pressure of $p = (2-3) \cdot 10^{-8}$ mbar at a sample temperature of 970 K for 1 h [5]. Under higher pressure $p = 3 \cdot 10^{-7}$ mbar the graphene layer can be formed within 3 min [6]. Here we report the use of a higher ketone like 3-pentanone as a precursor molecule, which yields better layers than we obtained by the use of the ethene precursor [15].

2. Experimental section

The experiments have been performed in a modified VG ESCALab (Electron Spectroscopy for Chemical Analysis) [16] under ultrahigh vacuum conditions. For XPS studies a monochromatised Al K_{α} X-ray source was used, providing photons with an energy of 1468.8 eV. The scanning tunneling microscopy experiments were carried out in a Park Scientific microprobe VPII instrument, attached to the same ultrahigh

vacuum system, using W tips. The Rh(111) single crystal was cleaned with repetitive cycles of Ar sputtering at a pressure of $p = 5 \cdot 10^{-5}$ mbar with an ion current density between 0.6 and 0.4 $\mu A/cm^2$ and annealing up to 1030 K. After each cycle an additional oxygen treatment was performed to burn residual carbon contaminations. The oxygen exposure was gradually reduced after each cleaning cycle from 29 to 6 L ($1 L = 1 \cdot 10^{-6}$ Torr s). The remaining oxygen was removed by flashing the crystal to a temperature of 1156 K. Before introducing 3-pentanone to the UHV system it was further purified by freezing/melting/pumping cycles. The graphene layer was formed by chemical vapor deposition of 3-pentanone at a pressure of $p = 2 \cdot 10^{-7}$ mbar, at a sample temperature of 1060 K. After a 10 min. exposure, corresponding to about 90 L, the sample was gradually cooled down (30 K/min) to room temperature.

3-pentanone is a carbohydrate ketone with the structural formula $CH_3-CH_2-CO-CH_2-CH_3$. An illustration of the molecule can be seen in Fig. 1. The molecule was chosen due to its favorable geometry, and bond strength hierarchy. The C O double bond is strongest and not expected to be broken during the reaction. Since the C–H bonds (4.3 eV) and the CH_3-CH_2 bonds (3.8 eV) are stronger than the $C_2H_5-C(O)C_2H_5$ bond (3.5 eV) we expect that this is the predetermined breaking point which releases upon dissociation of 3-pentanone two C_2H_5 radicals that act as dimer building blocks for graphene, while the carbonyl and the hydrogen desorb in the form of CO and H_2 and are pumped away. On clean Rh(111) the CO and the H_2 desorption temperatures are 510–540 K [17] and 410–490 K [17], respectively. A tentative illustration of this process is sketched in Fig. 1b). The details of the graphene formation process were not further studied within this work, though the resulting high quality single layer graphene sheets are an a posteriori justification of 3-pentanone to be an excellent precursor molecule for graphene growth.

3. Results and discussion

In Fig. 2 Al K_{α} X-ray photoelectron spectra of a *g*/Rh(111) preparation are shown. The overview in Fig. 2a) indicates that the

* Corresponding author. Tel.: +41 44 635 59 62.

E-mail address: roth@physik.uzh.ch (S. Roth).

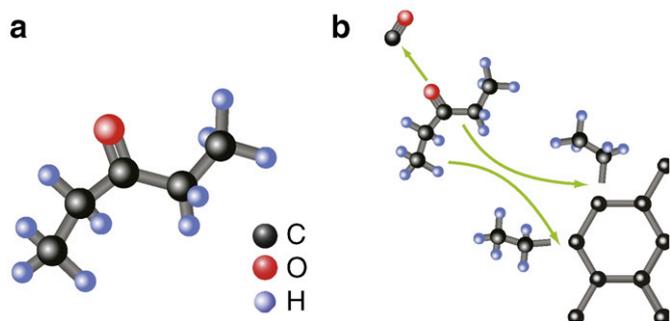


Fig. 1. a) Sketch of the 3-pentanone molecule, which has been used as a precursor to grow graphene. b) Tentative illustration of the graphene formation process. The pentanone molecules break into radicals on the hot rhodium surface. C–C units build graphene, while at 1000 K the remaining C=O and hydrogens do not stick on the surface.

surface consists of carbon and rhodium. The carbon coverage of the sample can be estimated from the C 1s and the Rh 3d_{5/2} photoemission yield. The intensity normalized with the atomic photoemission cross sections leads an atomic ratio $A_C/A_{Rh} = 0.40 \pm 0.02$. This number is in line with the atomic ratio of a *h*-BN nanomesh on rhodium, where the growth is self terminated after a single layer [18]. If the atomic ratio $(A_B + A_N)/A_{Rh}$ of 0.43 is normalized with the unit cell sizes of *h*-BN and graphene, respectively, we find a carbon coverage that corresponds to 0.96 ± 0.05 layers of graphene. In Fig. 2b) and c) the O 1s and the C 1s core levels are shown. The C 1s spectrum displays a

peak at a binding energy of 284.8 eV. This is in agreement with the high resolution XPS data on *g*/Rh(111) of Preobrajenski et al. [5]. Our instrumental resolution of 0.5 eV does not resolve the double peak in the C 1s spectrum that indicates high and low regions of *g*/Rh(111) [5]. No signature of CO is found, neither an O 1s signal nor a C 1s carbonyl-peak between 285.5 and 286 eV binding energy [19]. The small shoulder in the O 1s region is a loss satellite 9 eV below the Rh 3p_{1/2} line, which is also found in Auger spectra [20]. The XPS results are a first indication for the decomposition of 3-pentanone and the desorption of the carbonyles and hydrogen when it is brought in contact with the hot rhodium surface, and the formation of a single layer of graphene.

In a next step we investigated the long range order of the structure by low energy electron diffraction (LEED). In Fig. 3a) the LEED pattern of a graphene layer on Rh(111) is shown, recorded at a kinetic energy of 80.3 eV. The rhodium principal spots are surrounded by the superstructure spots that can be expressed with fractions of the principal spots. The high epitaxial quality of the graphene layer is reflected in the additional higher order superstructure spots around the first order spots. The intensity profile along the indicated line is shown in Fig. 3b). The lattice constant $N \cdot a_{sub}$ of the graphene superstructure is given by the ratio between the distance of the superlattice and the substrate spots. N is found to be 11.2 ± 0.5 , which corresponds with $a_{sub} = 0.269$ nm to a super lattice constant of 2.93 ± 0.13 nm. This is in agreement with a commensurate 12×12 on 11×11 periodicity of the superstructure as found in Ref. [4].

The exposure of rhodium to 3-pentanone leads to a large area growth of single layer graphene. Fig. 4a) shows a constant current scanning tunneling microscopy (STM) image of a large area of the

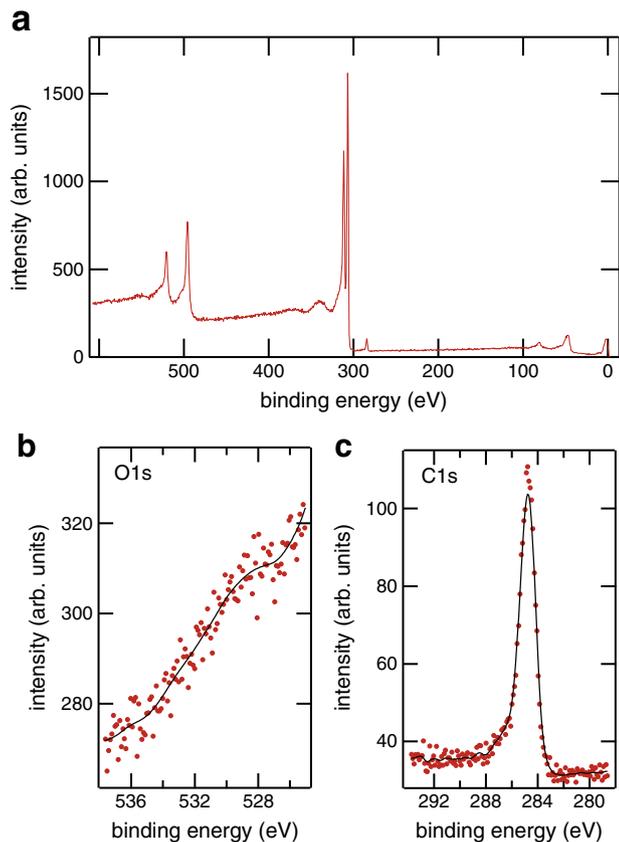


Fig. 2. Al K_{α} ($\hbar\omega = 1486.6$ eV) X-ray excited photoemission of a graphene layer on rhodium: (a) survey spectrum. (b) Close up on the O 1s core level. The shoulder at a binding energy of 529 eV corresponds to an intrinsic excitation of rhodium. (c) Close up on the C 1s core level spectrum. The black solid lines are a guide to the eye (10 point smooth).

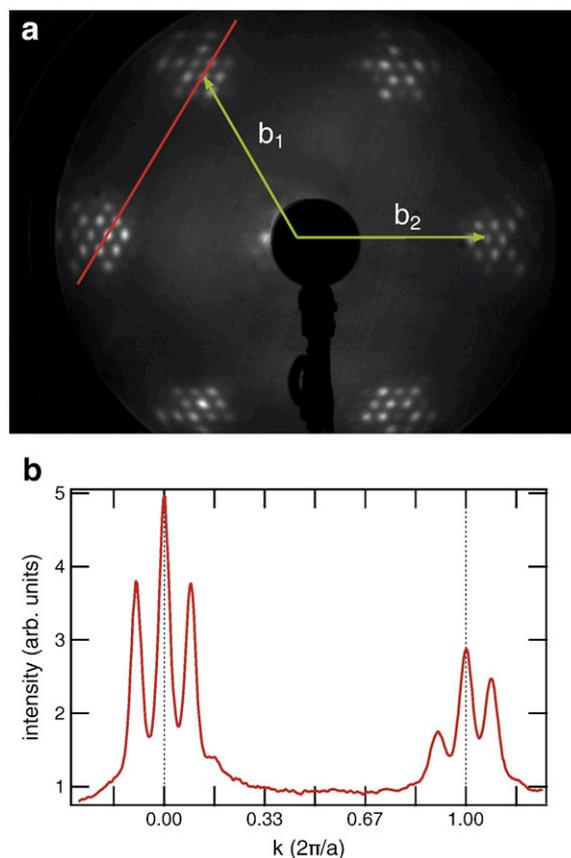


Fig. 3. a) LEED image of a graphene layer on Rh(111) at a kinetic energy of 80.3 eV. The reciprocal 1×1 lattice vectors b_1 and b_2 are indicated. b) Intensity profile along the indicated line in (a). The Rh–Rh nearest neighbor distance is $a = 0.269$ nm.

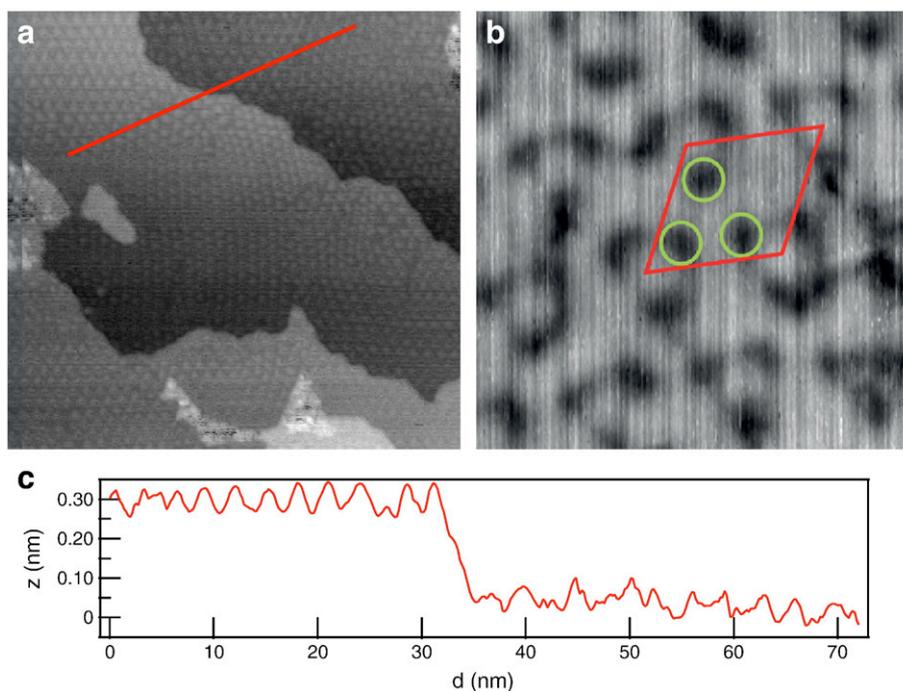


Fig. 4. Constant current STM image of a graphene layer on Rh(111). $I_{\text{tunnel}} = 1$ nA, $V_{\text{tunnel}} = 1$ V, scanning direction: vertical. (a) Large area 100×100 nm, and (b) close up: 10×10 nm. Areas close to the Rh substrate are dark. The corrugation at these tunneling conditions is 0.12 nm. Panel (c) shows a height profile along the indicated line in (a).

graphene layer that was synthesized on rhodium (111) [21]. The growth is nearly free of defects. The layer has a unique surface corrugation, which has previously been observed [4,6,7], and which is different from other transition metals such as Ru [10,12,22] or Ir [23]. Fig. 4b) shows a close up of the graphene unit cell. The unit cell is marked with a red rhomb. The superlattice constant is measured to be 3 nm, and is in agreement with an 11×11 unit cell. The corrugation, i.e. peak to peak amplitude is 0.12 nm. It is determined from a histogram of the vertical tip positions in Fig. 4b). A special feature in the corrugation of the $g/\text{Rh}(111)$ supercell are three pockets with a diameter of roughly 1 nm (green circles). This additional structure was identified to have a low local work function [6], and it will be interesting to further explore the influence of this feature on the template function [2], which is, based on these details, expected to be different to that of e.g. $g/\text{Ru}(0001)$.

4. Conclusions

In summary it has been shown that epitaxial graphene monolayers can be grown by means of chemical vapor deposition of 3-pentanone on Rh(111). A highly regular, corrugated superlattice was observed with a lattice constant of 2.93 ± 0.13 nm. XPS data indicate a single graphene layer on the rhodium surface. The corrugation of the graphene layer has three pocket-like areas, which could act as molecule traps, when using graphene on rhodium as a template for molecular self-assembly. Given the favorable performance of 3-pentanone as a precursor molecule, we expect that it will also apply for other substrates.

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