Graphene grown from flat and bowl shaped polycyclic aromatic hydrocarbons on Cu(111)

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Abstract: The growth of carbon layers, defective graphene and graphene by deposition of polycyclic aromatic hydrocarbons (PAHs) on Cu(111) is studied by scanning tunneling microscopy and X-ray photoelectron spectroscopy. Two different PAHs are used as starting materials: the buckybowl pentaindenocorannulene (PIC) which contains pentagonal rings and planar coronene (CR). For both precursors, with increasing sample temperature during deposition, porous carbon aggregates (350°C), dense carbon layers (400 – 450°C), disordered defective graphene (500°C – 550°C) and extended graphene ($\geq 600^\circ\text{C}$) are obtained. No significant differences for defective graphene grown from PIC and CR are observed. C 1s X-ray photoelectron spectra of PIC and CR derived samples grown at 350 – 550°C exhibit a characteristic C–Cu low binding energy component. Preparation at $\geq 600^\circ\text{C}$ eliminates this C–Cu species and only C–C bonded carbon remains.

Introduction

Structural defects in graphene^[1] are of high interest for metal-free catalysis,^[2] sensing and separation of small gaseous molecules,^[3,4] band gap tuning,^[5,6] spintronics^[7] or batteries.^[8,9] In addition, there is profound theoretical interest in localized defects^[10–13] and grain boundaries^[14,15] in graphene. Defects can be prepared from pristine graphene by electron beam irradiation,^[6,16,17] ion bombardment^[7,18–21] plasma etching^[4] or simply growth at moderate temperatures.^[22,23] On metal surfaces with low bulk solubility of carbon (e.g. Cu), graphene is grown with carbon stemming from simple gaseous hydrocarbons,^[24–28] solid carbon sources,^[29] or polycyclic aromatic hydrocarbons (PAHs).^[30,31] In contrast to defect-free graphene, which is generally obtained at high temperatures,^[24,32] only few studies focus on the growth of graphene and defective graphene at moderate temperatures.^[33,34] For graphene grown from methane on Cu(111) at 800°C, scanning tunneling microscopy (STM) reveals the formation of carbon clusters and periodically defective graphene.^[35] Growth at higher temperatures leads to defect-free extended graphene domains. A recent report showed that, due to relative differences in the stability of dehydrogenated aggregates formed by different precursors, graphene is formed on Cu foils by annealing of para- and meta-terphenyl but not by ortho-terphenyl.^[36] Furthermore,

the choice of PAH used as precursor, either coronene (CR), pentacene or rubrene, is reported to affect the quality of graphene sheets grown on polycrystalline Cu at 1000°C.^[31] More defects in graphene prepared from pentacene and rubrene compared to graphene prepared from CR were found using Raman spectroscopy. In contrast to the predominant view that graphene growth on Cu proceeds via dissociation of the precursor,^[37] the above cited results suggest that the structure of the molecular precursor might play a role in graphene growth. Also quantum molecular dynamics simulations starting from C₂ vs. CR precursors on Ni(111) find differences in intermediate graphene growth steps.^[38] To this end, this study compares the growth stages of defective graphene and graphene obtained with two different PAHs as precursors. In this work, defective graphene refers to carbon layers which contain nanometer sized graphene domains but also a high amount of structural defects. If parts of the structure of the precursor could be integrated into graphene, the synthesis of theoretically predicted two-dimensional carbon allotropes such as pentagraphene^[39,40] or Haeckelites^[41] may be possible.

Here, the transformation of two different molecular precursors (Scheme 1), pentaindenocorannulene^[42,43] (PIC, C₅₀H₂₀) and CR (C₂₄H₁₂) on Cu(111) into defective graphene and graphene is presented. Unlike CR, which consists of seven hexagons and can be considered (after dehydrogenation) as a subunit of graphene, PIC is a geodesic polyarene which also has 6 pentagons in its carbon backbone. The samples are prepared in ultra-high vacuum by sublimation of the precursors onto the substrate surface kept at specific temperatures and analyzed *in-situ* using X-ray photoelectron spectroscopy (XPS) and STM.

Scheme 1. Structures of precursors for graphene growth: pentaindenocorannulene (PIC) and coronene (CR). Pentagonal rings are highlighted in red, hexagonal rings in blue. PIC is dome-shaped and CR is planar.

Results and Discussion

Figure 1 and 2 show STM images of different length scale of samples produced by sublimation of PIC and CR on Cu(111) kept at different temperatures. Deposition of PIC onto the surface kept at 350°C (Figure 1a and 2a) leads to interconnected, fractal-like porous 2D structures growing predominantly from step edges. Internally, the aggregates consist of PIC-sized merged lobes. For pentacene annealed on

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Cu(111),^[44] similar covalent networks consisting of elongated, pentacene-like lobes were reported. Thus at this temperature the structure of the precursor is still partly preserved, although partial C–C has probably also already occurred. Preparation with PIC deposited at 400°C and 450°C (Figure 1b,c) leads to dense, corrugated carbon layers. Due to the high corrugation, no high-resolution images were obtained on these samples. Growth at 550°C (Figure 1d and 2b) leads to layers consisting of dark trenches pinned to the Cu substrate and flat areas, which correspond to small graphene domains. Growth at 600°C (Figure 1e) results in graphene domains with a bigger average size and fewer bright protrusions. The long ridges corresponding to domain boundaries and localized defects seen in the high-resolution images (Figure 2c,d) are discussed later. Preparation at 650°C and 700°C (Figure 1f, Figure S1) leads to extended graphene domains.

With CR as precursor, growth at 350°C (Figure 1g and 2e) leads to porous aggregates growing from the step edges, similar to the case of PIC. Also here, the size and shape of the lobes is consistent with that of CR. STM images obtained after growth at 450°C (Figure 1h and 2f) show the further transformation of molecules into a dense carbon layer. As in case of PIC, the porous layer has disappeared and a corrugated surface along step edges is observed. Growth at 600°C (Figure 1i and 2g) results in extended graphene flakes, like in case of PIC.

On all samples, vague features or streaks are imaged. This is ascribed to mobile molecules and also is the reason why the bare substrate appears with a similar height as the PIC and CR derived carbon aggregates prepared at 350°C (Figure 2h). In samples prepared at higher temperatures, less streaks are observed, presumably due to either desorption of this species or its conversion to graphene.

Figure 1. STM images of carbon layers grown by deposition of PIC (a-f) and CR (g-i) at different sample temperatures. (a,g) Dendritic aggregates observed after growth with PIC and CR at 350°C. (b-c, h) Deposition of PIC and CR at temperatures ranging from 400 – 450°C leads to dense layers with progressively larger graphene domains and fewer topographically high features. (d-f, i) Deposition of PIC and CR at 550 – 650°C leads to graphene and defective graphene layers with progressively fewer dark trenches. Imaging parameters: a) 330 pA, 22 mV; b) 330 pA, 24 mV; c) 220 pA, 32 mV; d) 330 pA, 24 mV; e) 110 pA, 23 mV; f) 490 pA, 22 mV; g) 210 pA, 29 mV, h) 410 pA, 23 mV; i) 530 pA, 29 mV. For visibility, in images (d,e,g,h) the contrast is folded at step edges.

Figure 2. Small scale STM images of carbon layers grown by deposition of PIC (a-d) and CR (e-g) at different sample temperatures. The brown and black circles represent the size of the PIC and CR precursors, respectively. (h) Line profiles taken at the scan lines indicated by light blue lines in (a-g). Imaging parameters: a) 280 pA, 22.3 mV; b) 310 pA, 20.1 mV; c) 270 pA, 28.4 mV; d) 250 pA, 23.5 mV; e) 290 pA, 35.3 mV; f) 250 pA, 36.3 mV; g) 490 pA, 25.9 mV. In image a) the image contrast is folded for visibility of the high features.

The chemical states of carbon for the different transformation stages of PIC and CR are analyzed by C 1s XP spectra (Figure 3a,b). The spectra were obtained at room temperature after deposition of the molecules on the substrate kept at the indicated temperatures. For PIC deposited on Cu(111) kept at 27 °C, the C 1s signal presents a peak centered at 284.6 eV. Graphene grown at 650 °C and 700 °C has a narrower C 1s signal centered at 284.8 eV, consistent with previously reported XP spectra of graphene/Cu(111).^[45] Interestingly, the samples grown at intermediate temperatures (350 °C – 550 °C) exhibit an additional C 1s signal at lower binding energy. In agreement with reported C 1s binding energies for carbon binding to Cu or Ag (283.1 to 284.0 eV),^[46–51] the low binding energy carbon species is identified as carbon interacting with the Cu substrate. For simplicity, we call this low binding energy species “organometallic carbon”^[51] although it most likely represents a number of different types C – Cu species.

The C 1s XP spectra of carbon layers grown from CR are very similar (Figure 3b) to the ones grown from PIC. CR deposited on Cu(111) kept at room temperature has a C 1s binding energy of 284.8 eV. The slight difference in binding energy and narrower line shape with respect to PIC is attributed to their different structure. For graphene grown from CR at 600 °C, the C 1s binding energy of 284.8 eV is identical to the one of graphene grown from PIC. Like in case of PIC-derived carbon layers, an additional C 1s signal at lower binding energies is present for carbon layers grown from CR at intermediate temperatures.

The C 1s spectra are deconvoluted by peak fitting with Voigt functions (50% Gaussian and 50% Lorentzian). The peak fits are constrained in order to reduce the number of free parameters: First, the binding energy (284.8 eV) and FWHM (1.3 eV) of graphenic carbon is determined from the 700 °C sample and kept

identical for the other spectra (dashed red arrow). Second, a organometallic component with identical fixed FWHM (1.3 eV) is fitted with the 450 °C PIC data where the low binding energy shoulder is most intense. This yields a binding energy of 284.1 eV for organometallic carbon which is then also kept fixed. Finally, the other PIC and CR spectra are fitted with the same two components, with the exception of PIC at 27 °C and 350 °C where the molecular C signal (binding energy 284.6 eV, FWHM 1.7 eV) instead of the graphenic one (284.8 eV) is used.

The fraction of organometallic C obtained by this analysis is shown in Figure 3c. It should be noted however, that the magnitude of the chemical shift between graphenic and organometallic carbon (0.7 eV) compared to the energy resolution (1.1 eV) limits the precision of this analysis.

The significant organometallic C–Cu fraction in PIC and CR derived samples prepared at 350 °C in combination with the presence of fractal aggregates (Figure 1 and 2) which still resemble the structure of the precursors, indicates that at this stage the aggregation is primarily induced by (non-specific) C–H activation *via* dehydrogenation, consistent with the literature.^[52–55]

In samples prepared at 400 °C to 550 °C, the C–Cu fraction reaches ~60%. This high organometallic peak fraction exceeds the fraction of carbon atoms which can undergo C–H activation (40% for PIC and 50% for CR) and thus indicates (unspecific) C–C bond breaking. This is consistent with STM data (Figure 1 and 2) which shows the formation dense carbon layers and defective graphene.

Interestingly, despite the presence of defective graphene domains in samples grown at 500 – 550 °C, the peak fraction of organometallic carbon remains high and drops only at 600 °C where the first extended graphene domains are observed. In

contrast, organometallic C–metal species produced e.g. by Ullmann chemistry are converted already at around 200 – 300°C to C–C bonds.^[46,47,50,51,56] Thus the growth dynamics at 400 – 550°C presumably involves an equilibrium between C–C and C–Cu bond formation and breaking. It is also likely that the dark trenches in between of defective graphene domains contribute to the C–Cu signal. However, it is important to note that the existence of mobile species in STM which also contribute to the C 1s XP signal, does not allow for a quantitative comparison of STM and XPS data.

Figure 3. C 1s XP spectra recorded after deposition of PIC (a) and CR (b) kept at the indicated temperatures. The spectra are deconvoluted into graphenic, organometallic and molecular carbon components with fixed binding energies and widths (see text). The * signs and the dashed arrows and lines indicate the components which have been fitted freely and the related components with fixed binding energies and widths. The XPS intensities are normalized for visibility. (c) Peak fraction of organometallic carbon.

High resolution STM images of defective graphene domains grown from both PIC and CR show localized defects (Figure 4). The trenches correspond to grain boundaries.^[1] The rotation of the graphene lattice by 12° is indicated by blue arrows. Three different kinds of localized defects can be observed (marked with red squares). Based on the very good agreement with simulated STM images discussed in refs. [12,57], the defects shown in Figure 4b and 4c are most likely i) flower defects (rotational grain boundary with symmetry consisting of six pairs of hepta- and penta-rings) and ii) Stone-Wales defects^[57] (two pairs of pentagonal and heptagonal rings). The defect shown in Figure 4c is most likely a point defect (e.g. vacancy^[58] or an incorporated heteroatom^[59]). Notably, localized defects also occur in graphene grown from CR (Figure 4e). Their distorted appearance is presumably related to an imperfect tip.

Conclusions

In summary, deposition of either PIC and CR on hot Cu(111) surfaces leads to carbon layers which can be qualitatively described as porous carbon aggregates (350°C), dense carbon layers (400°C – 450°C), defective graphene consisting of nanometer sized graphene domains (500°C – 550°C) and extended graphene ($\geq 600^\circ\text{C}$). In view of the different appearance with respect to carbon aggregates grown from pentacene,^[44] in the porous aggregate regime (350°C) the precursors are still partly preserved. At higher temperatures, no significant differences of the carbon structures grown from PIC and CR are apparent. No haecelites, pentagraphene or ordered defective graphene^[35] are obtained. Local defects are found both in PIC and CR derived graphene.

Figure 4. Graphene layers grown from PIC and CR containing localized defects. Images (a-d) were obtained after deposition of PIC onto Cu(111) kept at 650°C and subsequent annealing at 600°C for one hour without further evaporation of molecules. Blue arrows label two rotational domains of produced graphene separated by grain boundaries. Three red boxes label the locations of three different local defects, shown in images (b-d) respectively. Image (e) is obtained after evaporation of CR onto Cu(111) kept at 600°C and subsequent annealing for 30 min. Blue arrows label the lattice directions at the grain boundaries. Imaging parameters: a) 390 pA, 22.9 mV; b) 1.15 nA, 24.4 mV; c) 49 pA, 22.8 mV; d) 62 pA, 23.5 mV; e) 240 pA, 27.5 mV.

Experimental Section

Sample preparation: The experiments were performed *in-situ* in ultra-high vacuum on Cu(111) (MaTeCK GmbH). The base pressure was 3×10^{-10} mbar. The substrate was cleaned by cycles of Ar⁺ ion sputtering and annealing. PIC (University of Zürich) and CR (Sigma-Aldrich, 99%, purified by resublimation) was sublimed from Knudsen cells onto the samples held at different temperatures. Different sublimation times (15 – 60 min) were chosen in order to obtain carbon layers with similar coverages. Unless specified otherwise, the samples were kept at a fixed, elevated temperature during deposition for 5 min after stopping the deposition before allowing them to cool down to room temperature.

X-ray photoelectron spectroscopy: XP spectra were measured at room temperature using non-monochromatic Al K_α X-rays in normal emission. The binding energy scale was calibrated on the clean Cu surface using the Cu 2p_{3/2} core level (932.7 eV) and the Fermi level (0.0 eV).

Scanning tunneling microscopy: STM images were acquired at room temperature in constant current mode and with a PtIr tip. The tip was mechanically cut and then sputtered by Ar⁺ ions *in-situ*. The STM images were processed using WSxM.^[60]

Acknowledgements

Financial support by the University of Zürich research priority program LightChEC and by the Swiss National Foundation (R'Equip, grant No. P300P2_177755) is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: graphene, copper surface, defective graphene, scanning tunneling microscopy, x-ray photoelectron spectroscopy

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Entry for the Table of Contents

ARTICLE

Sublimation of planar and bowl-shaped precursors on a copper surface kept at elevated temperatures leads to carbon layers with varying morphology: porous aggregates, disordered and dense carbon layers, defective graphene and extended graphene.

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