Bandgap formation in graphene on Ir(111) through oxidation.

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Abstract

A graphene monolayer on single crystal Ir(111) has been studied using angle-resolved photoemission spectroscopy (ARPES) before and after exposure to atomic oxygen. With increasing oxygen coverage the Dirac cone, centered on the K-point of the Brillouin zone, broadens and finally transforms to a parabolic rather than linear feature, introducing a pronounced energy bandgap at the Fermi level. The opening of a gap of around 0.35 eV in the occupied density of states was observed at the highest exposure time.

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1. Introduction

Graphene needs almost no introduction since the awarding of the 2010 Nobel prize in physics for the seminal work of Geim and Novoselov of 2004 [1]. Indeed, its unique properties have inspired research efforts in fundamental science as well as novel electronic devices in a major way [2]. And yet, to fully harness the power of graphene, the ideal conduction properties of graphene need to be disturbed in order to obtain a (tunable) band gap and thereby achieve semiconducting behaviour. One way is to attach (covalently) bound species, such as H, O or F to the surface of graphene [3, 4, 5]. This is also known from graphene oxide (GO), which is an insulator accommodating several oxygen species (*e.g.*, C=O, C-O-C, COOH, OH) on both the basal planes and the edges of flakes as it is often prepared chemically, ex-situ [6, 7]. In contrast, when graphene

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oxidation is studied on a metal substrate under ultra-high-vacuum (UHV) conditions, no hydrogen containing species are found, and edge effects are strongly reduced. This is especially true for graphene grown on iridium, which allows for a nearly perfect monolayer graphene (MG) coverage and, in fact, oxidation produces only epoxy groups [10]. On free-standing, flat graphene oxygen would energetically prefer to organize in rows of epoxy bridges [8], but this is hard to realize experimentally when defects and micro-corrugation of loose sheets would govern the most likely adsorption sites and seriously disturb ordered patterning. Instead, the moiré pattern of MG/Ir(111) offers a structural template for oxygen adsorption which allows for ordered adhesion and therefore has a better chance to preserve the periodicity and hence the dispersion relations of the valence band, similar to hydrogen adsorption on MG/Ir(111) [9, 11].

2. Experiment

Angle-resolved photoelectron spectroscopy (ARPES) measurements were performed at beamline I4 of the MAX IV laboratory, Lund, Sweden. The experimental chamber (base pressure $3 \cdot 10^{-10}$ mbar) is equipped with a SPECS Phoibos-100 analyzer with 2D-CCD detector. A photon energy of 36 eV was used for all ARPES measurements. All experiments were performed at room temperature (RT) with an angular resolution better than 0.8° . At each oxygen exposure, several band profiles were collected in order to ensure that the K-point, *i.e.*, the point which should have the smallest gap, was found. The Fermi level of the Ir substrate was used to pinpoint zero binding energy in each measurement. It is not visible in the figures as a result of setting intensity limits to emphasize the graphene π -band. Low energy electron diffraction (LEED) pictures were taken at 60 eV beam energy on similarly prepared films in a separate vacuum chamber. MG/Ir(111) was prepared through cracking of propene on a hot Ir(111) surface cleaned in UHV, the details have been outlined elsewhere [10]. Oxygen exposure of the MG/Ir(111) was performed at RT by atomic oxygen produced in a cracker source (MBE-Komponenten) equipped with a shutter. The cracker was operated at $T = 1650^\circ\text{C}$ and an oxygen partial pressure of $1 \cdot 10^{-7}$ mbar. The distance between sample and cracker was approximately 10 cm, implying that similar (saturation) exposure times as in Ref. [10] should apply.

3. Results and discussion

Fig. 1a shows the bandstructure around the K-point of the Brillouin zone as observed in ARPES measurements on clean MG/Ir(111). The linear π -band dispersion, culminating in the Dirac point close to the Fermi level EF, is in close agreement with previous reports, including the formation of minigaps around 0.7-0.8 eV, associated with the moiré pattern [12].

Upon exposure to atomic oxygen, with times as indicated in Fig. 1b,c, the π -band first broadens and the intensity maximum starts to shift away from the

Fermi level before a real gap is opened. Simultaneously, the weakening of the minigap structure indicates that the long range moiré order is reduced. This is also confirmed by the LEED image taken after 9 min. exposure (depicted in Fig. 2b), as compared to the more complete moiré pattern of the pristine MG/Ir(111) surface shown in Fig. 2c. Importantly, traces of the graphene moiré structure in the LEED pattern can be observed, even after 30 minutes exposure (not shown), but are substantially blurred. The effect on the band structure is even more severe, and after 15 minutes (Fig. 1d) the band is hardly visible, broadened considerably and heavily distorted. The dotted lines in Fig. 1a and d are a guide to the eye and indicate that, between the pristine and our most oxygen saturated MG/Ir(111) surface, the nature of the dispersion has shifted from a linear appearance to a more parabolically rounded apex and a gap of around 0.35 eV has opened up. From STM and core level photoemission measurements we know that initial oxygen adsorption favors the formation of epoxides in the pores (lower lying regions of the moiré structure), accompanied by an increased bonding between the substrate and those C atoms that are not bonded to O. All in all, this leads to an increased sp^3 -like bonding environment of the carbon atoms [10]. On freestanding graphene the formation of an epoxy group stretches the underlying C-C bond, away from the two-dimensional structure. On MG/Ir(111) this is somewhat analogous to the oxygen adsorption on the protruding wire regions. Formation of epoxy groups involving sp^3 -like C atoms hybridization is therefore responsible for significant disturbance of the π -conjugated system of the sp^2 -hybridized C atoms, hence introducing a parabolic band shape and the energy gap into the graphene "honeycomb-structure"-derived π band. The loss of photoemission intensity in the bands and increased broadening in the spectra, however, testifies that there is no preference for a strict long range order, such as the formation of neatly aligned epoxy bridges, in the adsorption [8, 13].

After annealing the sample for 5 min at 500°C the original band profile is largely restored, albeit a bit weaker, and with its intensity maximum (Dirac point) closer to the Fermi level, as depicted in Fig. 2a. This could be the result of the defects in the form of tiny etched holes that are created (mainly in the wire regions) when the oxygen leaves the surface [10]. This definitely disturbs the long range periodicity, observed as blurring, and could also mean an increased p-type doping effect.

4. Conclusions

The opening of a bandgap at the K-point of the Brillouin zone of MG on Ir(111) through controlled oxidation in UHV has been measured and quantified. At its largest extent (15 min oxidation) the gap is about 0.35 eV and is accompanied by a significant broadening. Although the overall structure of the π -band remains intact, its shape after oxidation is more reminiscent of a parabola than of the linear dispersion in pristine graphene. Upon annealing the graphene is able to recover substantially, including the reappearance of the minigaps, yet showing more density of states at the Fermi level.

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Figure 1: Photoemission intensity around the K point of the Brillouin zone of graphene on $\text{Ir}(111)$ (wavevector direction as indicated in the inset). a) Clean graphene, b) after 3 min. exposure to atomic oxygen, c) after 6 min., and d) after 15 min (approaching saturation).

Figure 2: a) Photoemission intensity after annealing (5 min, 500°C) of the oxygen saturated sample. b) LEED image taken on graphene on Ir(111) after 9 min exposure to atomic oxygen, compared to c) clean graphene.