

Oxygen Switching of the Epitaxial Graphene-Metal Interaction

Paolo Lacovig¹, Rosanna Larciprete², Søren Ulstrup³, Matteo Dalmiglio¹, Marco Bianchi³, Federico Mazzola³, Liv Hornekær³, Fabrizio Orlando⁴, Alessandro Baraldi⁴, Philip Hofmann³, and Silvano Lizzit¹

¹Elettra-Sincrotrone Trieste, S.S. 14 Km 163.5, 34149 Trieste, Italy

²CNR-Institute for Complex Systems, Via Fosso del Cavaliere 100, 00133 Roma, Italy

³Department of Physics and Astronomy, Interdisciplinary Nanoscience Center, Aarhus University, 8000 Aarhus C, Denmark

⁴Physics Department and CENMAT, University of Trieste, Via Valerio 2, 34127 Trieste, Italy and IOM-CNR Laboratorio TASC, Area Science Park, S.S.14 Km 163.5, 34149 Trieste, Italy.

paolo.lacovig@elettra.trieste.it

Abstract

The mass production of graphene (GR) based electronic devices requires the synthesis of high quality, i.e. with low defects concentration, and large area GR layers. Among the different methods that can be used for GR preparation, epitaxial growth on transition metal surfaces is one of the most promising techniques to achieve high quality GR layers. The interaction with the substrate, however, is the major drawback of epitaxial GR [1]. In some cases, e.g. GR layers grown on Ru(0001), Rh(111) or Re(0001), this interaction can be sufficiently strong to prevent the typical electronic properties of GR from being established. On the other hand, a very weak interaction, e.g. GR on Pt(111), leads to the formation of GR domains with different orientations. GR/Ir(111) is a representative example of a weakly bound interface: GR-like electronic properties are observed but the moiré pattern due to the lattice incommensurability between GR and its substrate gives rise to replica bands and minigaps close to the Fermi level. It appears thus difficult to achieve a weak interaction with high structural quality at the same time. A possible solution is the epitaxial growth of GR on a sufficiently interacting substrate, such as Ir(111), and the subsequent decoupling by the intercalation of metals, silicon, fluorine or hydrogen in order to restore, at least partly, the pristine linear band dispersion.

Oxygen intercalation appears as a viable route to decouple GR/metal interfaces, but so far intercalation has been demonstrated only for incomplete monolayers or islands [2]. Here, using high-resolution fast x-ray photoemission spectroscopy (XPS) with synchrotron radiation, we show that oxygen intercalation is achieved on an extended layer of epitaxial GR on Ir(111), which results in the “lifting” of the GR layer and in its decoupling from the metal substrate [3]. Below GR oxygen adsorption on the substrate proceeds as on clean Ir(111), the main difference being a slightly higher oxygen coverage. Upon lifting, the C 1s signal shows a downshift in binding energy, due to the charge transfer from GR to the electronegative oxygen. Moreover, the characteristic spectral signatures of the GR-substrate interaction in the valence band are removed, and the spectrum of strongly hole-doped, quasi free-standing GR with a linear π -band dispersion is observed. Temperature programmed fast-XPS measurements pointed out that abrupt oxygen deintercalation with a slight carbon etching occurs around $T=600$ K. After deintercalation, GR restores its interaction with the Ir(111) substrate. Additional intercalation/deintercalation cycles readily occur at lower oxygen pressure and temperature, consistently with an increasingly defective lattice. Our findings demonstrate that oxygen intercalation is an efficient method for fully decoupling an extended layer of GR from a metal substrate. They pave the way for the fundamental research on GR, where extended, ordered layers of free-standing GR are important and, due to the stability of the intercalated system in a wide temperature range, also for the advancement of next-generation GR-based electronics.

References

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