Towards integrated atomically smoothed graphene nanoribbons devices.

Marc NUÑEZ, Sébastien LINAS, Miguel RUBIO ROY, Caterina SOLDANO,
Philippe SALLES, Olivier COUTURAUD and Erik DUJARDIN

NanoSciences Group, CEMES CNRS UPR 8011
29 rue J. Marvig, BP 94347, 31055 Toulouse Cedex 4, FRANCE
nunez@cemes.fr, dujardin@cemes.fr

Abstract

The growing interest in graphene stems from the specific properties gathered by this atomically thin sheet of carbon atoms that address a number of technical or scientific locks in fields as diverse as mesoscopic physics, transparent electrodes, electromechanical and optical devices, heat transport, sensors, etc... Graphene offers a direct and stable access to a one-atom thick 2D membrane in which and atomically precise structures can be engineered provided that its lateral confinement is carefully controlled. It appears that the topology and structural quality of this patterning (e.g. nanoribbons) from the mesoscopic to the molecular scale strongly influences the corresponding electronic properties. In spite of numerous approaches and significant progress, graphene patterning at multiple length scales down to a few nanometers while preserving its pristine quality is one of the main challenges.

Indeed, several graphene nanopatterning techniques, yielding for example nanoribbons, have been investigated so far, which rely on e-beam or optical lithography followed by reactive ion etching, [1] direct milling using a focused ion beams, [2] chemical cutting with free or guided catalytic nanoparticles.[3] While well-suited for multiscale patterning of arbitrary designs, these techniques have been shown to introduce contamination (resists, implanted ions, metal adsorbates,....) and to induce severe amorphization along the graphene edges which practically prevents the production of nanometer-scale features in pristine graphene. Alternative top-down approaches to produce graphene ribbons consist in tearing graphene, possibly along preferential crystallographic directions by extensive ultrasonication [3] or carbon nanotube opening.[4] Recent bottom-up approaches to graphene nanoribbons have reached the ultimate edge precision by polymerizing polyaromatic precursors into ribbons of atomically precise edge structure.[5] However, transport properties can only be studied by scanning tunneling microscopy as device production from these extremely narrow ribbons still face challenges such as contact resistance and multi-scale integration.

In this context, we propose to combine low energy electron beam and chemical etching to design arbitrary graphene patterns of sub-10 nm feature size and crystalline edges. Our approach is compatible with ultra-high vacuum (UHV) environment and applicable to connected device fabrication.

Our graphene nanopatterning technique consists in inducing a localized chemical etching with a focused electron beam. The electron beam activates a chemical reaction between graphene and the injected gas. This allows low energy electrons to produce holes in graphene lattice well below the 86 kV knock-on energy threshold of electron beam etching in vacuum.[6] The programmed raster scanning of the SEM electron beam allows etching an infinite variety of arbitrary patterns. [7, 8]

The presentation will detail the parameters controlling the etching performances such as the dose analysis, influence of the substrate or sample thickness and will show that it easily enables to etch multi-micrometer-long cuts as well as sub-10 nm features in monolayered graphene (Fig. 1a). This ability to multi-scale patterning is a key feature to the integration of quantum devices to mesoscopic sizes that allows macroscopic transport measurements.

We will present spherical aberration corrected transmission electron microscopy investigation of cut edges and graphene nanoribbons and show that the edges produced by our technique appear to be crystalline and atomically smooth (Figs. 1b-c). The amorphous carbon pollution induced during the patterning is almost absent and graphene in direct proximity of the pattern edges is free of lattice amorphization.

Our approach has also been adapted to device configuration. To this end, micromechanically exfoliated graphene is deposited on silica substrates perforated with 1x5 µm pools (Figs. 1d-e). The etching procedure has been successfully adapted to this partially suspended graphene and graphene nanoribbons with length of several hundred of nanometers and width below 50 nm are routinely produced (Fig. 1f).

Finally transport measurements performed on suspended graphene nanoribbons with crystalline edges will be discussed.

References

[1] Chen Z et al. *Physica E (*2007) 40, 228; X. Wang et al., Phys, Rev. Lett. (2008) 100, 206803; M. Y. Han, J. C. Brant, P. Kim, *Phys. Rev. Lett.* (2010) 104, 056801
[2] J.F. Dayen et al. *Small* (2008) 4, 716; M. C. Lemme, et al. ACS Nano (2009) 3, 2674
[3] Campos et al. Nano letters (2009) 9, 2600
[4] H. J. Dai et al., Nature (2009) 458, 877; J. M. Tour et al., Nature (2009) 458, 872
[5] K. Mullen, R. Fasel, et al. Nature (2010) 466, 470; Koch, M., et al. Nature Nanotech. (2012) 7, 713
[6] Girit et al. *Science* (2009) 323, 1705
[7] S. Linas, M. Nunez, M. Rubio-Roy, C. Soldano, R. Arenal, P. Salles, O. Couturaud, A. Miranda, E. Dujardin, in press
[8] M. Nunez, M. Rubio-Roy, R. Arenal, P. Salles, E. Dujardin, in preparation

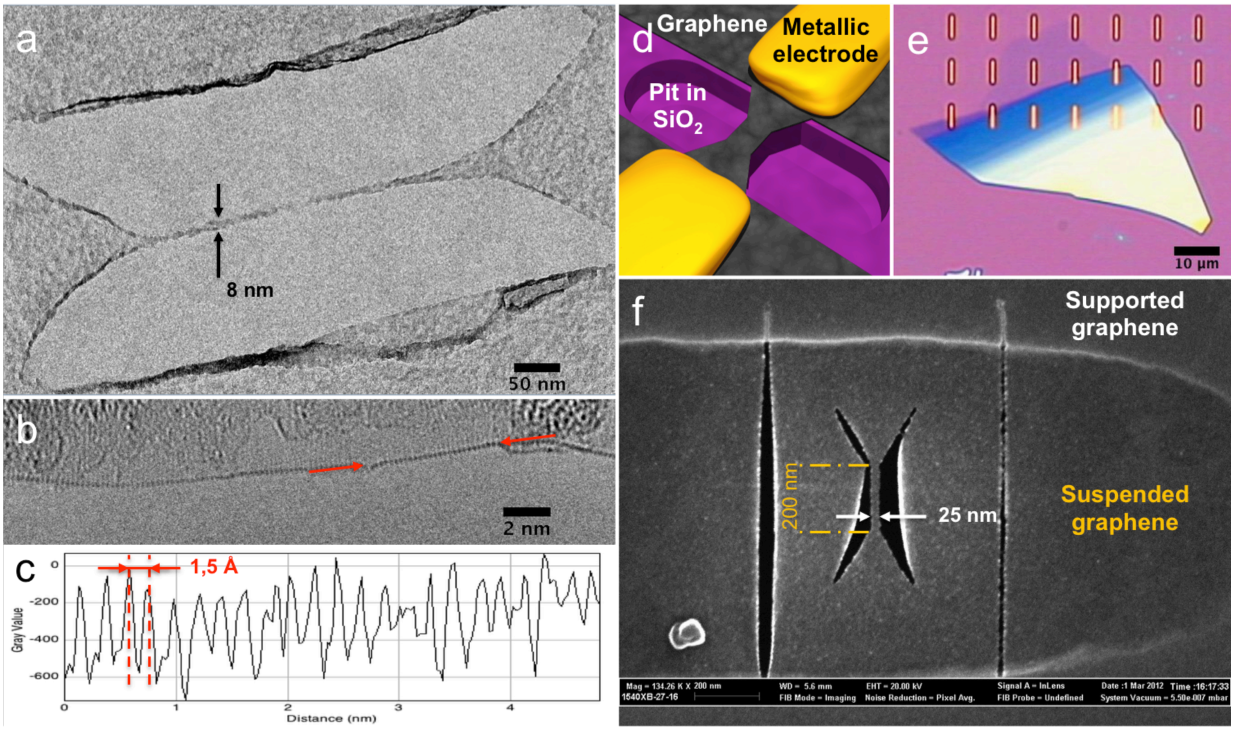

Figure1. (a) Transmission electron microscopy (TEM) image of a 320x8 nm graphene nanoribbons (GNR) etched in monolayer graphene using gas-assisted electron beam etching. (b) Spherical aberration corrected TEM image of a GNR edge showing the crystalline and atomically smooth rim devoid of amorphous carbon adsorbates. (c) Intensity profile measured between the arrows in (b). The distance between successive interference spots (1.5 Å) is commensurate with either zig-zag or armchair edge. (d) Schematic representation of a GNR device partially suspended above a micrometric pool etched in the Si/SiO2 substrate. (e) Optical micrograph of micromechanically exfoliated graphene deposited on top of Si/SiO2 substrates patterned with arrays of 250 nm deep, 1x5 µm pools. (f) Scanning electron micrograph image of a 200x25 nm GNR etched in partially suspended graphene. [7, 8]