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Fabrication of highly regular suspended graphene nanoribbons through a one-step electron beam lithography process

Miquel López-Suárez [a,1,2], Francesc Torres [a,2], Narcís Mestres [b,3], Riccardo Rurali [b,3], Gabriel Abadal [a,*]

[a] Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Barcelona, Spain
[b] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de Bellaterra, E-08193 Bellaterra, Barcelona, Spain

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ABSTRACT

A method to obtain pre-oriented large longitudinal 1-D arrays of identical suspended graphene nanoribbons is presented. Mechanical exfoliation from graphite was done in order to deposit single- and multiple-layered graphene over a Polymethyl-Methacrylate (PMMA) substrate, which is used as a sacrificial material. Electron beam lithography (EBL) is used to define the anchors and the suspended part of the structures. The method allows achieving a high number of graphene suspended nanoribbons with a very regular width and length. The main advantage of the method, from the process point of view, with respect to other standard procedures is that only one EBL step is needed in the whole sequence, so that the overall process is extremely simplified.

1. Introduction

Graphene, among other 2D-structured materials, has attracted the attention for the last years of both experimental and theoretical researchers due to its outstanding mechanical [1–3] and electrical [4] properties. In particular, a lot of efforts have been devoted to the fabrication and characterization of graphene-based-nanoelectromechanical systems (NEMS) [5–9]. Graphene sheets can be obtained through chemical growth [10,11] or mechanical exfoliation of a primary graphite stack [12]. The latter is very common thanks to its simplicity, though its drawbacks are the low probability of obtaining single-layer graphene ribbons and the high shape variability they present from flake to flake, hindering the achievement of reproducible results for different ribbons and the systematic study of the properties of graphene-based NEMS.

Here we present a simple fabrication method that maximizes the probability of obtaining mono and bi-layered graphene (usually around 0.13%, or a total graphene area of 0.13 mm^2 per square centimeter of exposed area) and to largely reduce their geometric variability, controlling the orientation and increasing the shape regularity of the ribbons. The proposed method simply requires a standard mechanical exfoliation and the transfer of graphene flakes on a Si/Cr/Au/PMMA substrate as initial step, followed by an EBL-based definition of large areas of nanotrenches on the PMMA layer at the flakes zone, to achieve suspended ribbons.

2. Fabrication process

A 20 nm/100 nm thick layer of chromium/gold is deposited on a 1 cm^2 p-type (100) silicon substrate 500 μm thick. 950 k molecular weight Polymethyl-Methacrylate (PMMA), 2% dissolved in anisole, is spun at 1500 rpm for 1 min. After spinning, the sample is baked in a hot plate to evaporate the anisole solvent at 180 °C for 1 min. The spinning/baking sequence is repeated 3 times in order to achieve a total PMMA layer 300 nm thick. Such a thickness will assure the suspension of the graphene structure once the sacrificial PMMA layer is removed. A scheme of the resultant stack can be seen in Fig. 1(a).

Mechanical exfoliation is done following a pseudo-standard procedure [12], which consists on separating several layers from a fresh HOPG graphite substrate by contacting with the adhering side of a scotch tape. Once some few layers thick graphite flakes have been transferred to the adhesive tape, they are brought under an iterative peeling sequence in order to reduce the number of layers and eventually yield graphene structures. Usually the peeling process, which is performed using flake-free areas of the tape, is

* Corresponding author. Tel.: +34 93 5813525; fax: +34 581 2600.
E-mail addresses: miquel.lopez@nipslab.org (M. López-Suárez), francesc.torres@uab.cat (F. Torres), narcis@icmab.es (N. Mestres), rrurali@icmab.es (R. Rurali), gabriel.abadal@uab.cat (G. Abadal).
[1] Present address: NiPS Laboratory, Dipartimento di Fisica, Università di Perugia, via A. Pascoli, 1, I-06123 Perugia, Italy. Tel.: +39 075 585 2733; fax: +39 075 5848458.
[2] Tel.: +34 93 5813525; fax: +34 581 2600.
[3] Tel.: +34 93 5801853.

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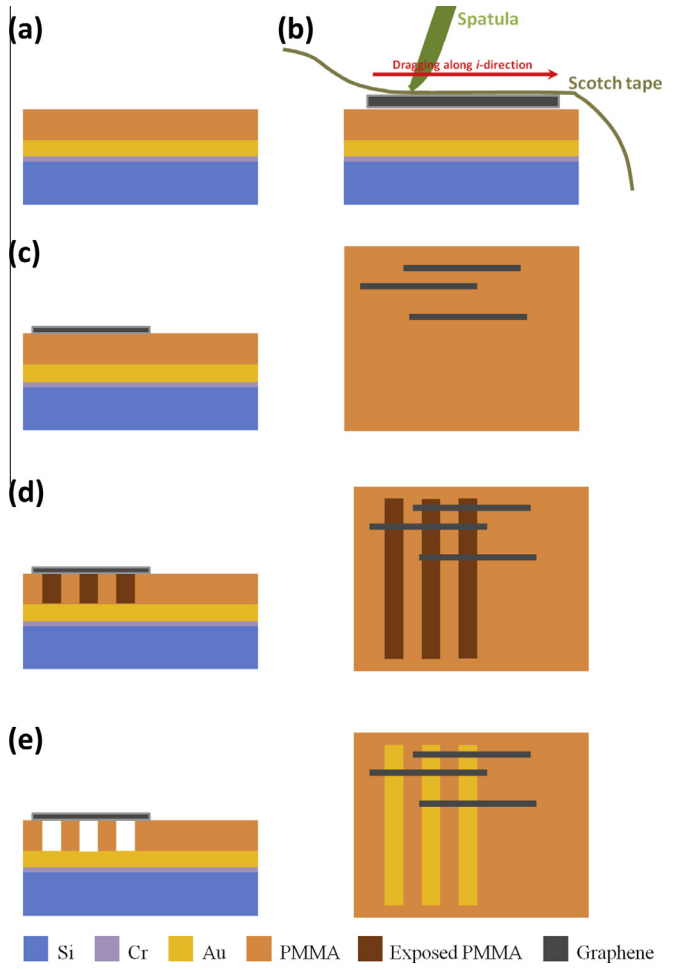

Fig. 1. Schematic representation of the fabrication process. (a) A stack of silicon (0.5 mm), chromium (20 nm), gold (100 nm) and PMMA (300 nm) is used as a substrate. (b) A non-abrasive spatula is used to favor the transfer along a certain direction. (c) A set of pre-oriented graphene ribbons are transferred onto the substrate. (d) The sample is exposed selectively to an EBL process to pattern the trenches. (e) The exposed PMMA is removed achieving the suspended devices. From (c) to (e), left and right figures correspond to cross-section and top-view of the sample, respectively.

repeated up to five times. After this process, the scotch tape becomes almost fully covered by layered regions ranging from graphene (almost indistinguishable light grey) to few-layer thick graphite (bright grey).

Once the mono and multilayered graphene flakes are attached to the scotch tape, the transfer is done pressing them onto the substrate and dragging a spatula following a certain *i*-direction, as represented on Fig. 1(b) and (c). As it will be later discussed, the probability of obtaining a high density of graphene ribbons depends on the chosen dragging direction. A special attention is paid during this transfer step in order to do not pull out part of the Cr/Au/PMMA layer when the adhesive areas of the tape that were not covered by flakes get in contact with the sample surface.

Trenches are dug under graphene by exposing the PMMA selectively with the electron beam of a FE LEO 1530 with Raith Elphy Plus attachment, using a beam energy of 20 keV and an electron dose of the order of 150 $\mu C/cm^2$, Fig. 1(d) and dipping the sample into a standard methyl isobutyl ketone/isopropyl alcohol developer, Fig. 1(e). After removing the exposed PMMA, the graphene ribbons get released and the underlying Au film becomes visible, allowing a good contrast for scanning electron microscopy (SEM) imaging. Different trench widths, that in turn determine the length of the suspended ribbons, are considered, i.e. 100, 300, 500 and 600 nm. Any special care has been taken to avoid the collapse of the structures right after the last PMMA developing step, since the length of the ribbons is not large enough.

3. Characterization of the devices

3.1. Scanning electron microscopy inspection

Fig. 2 shows SEM images of two processed samples, where some graphene flakes (horizontal structures) on the trench patterned PMMA surface (vertical strips) are visible. Trenches have been defined with different widths depending on the sample, but those in Fig. 2(a) and (b) correspond to a width value of 500 nm and those in Fig. 2(c) and (d) have three different widths: 100, 300 and 600 nm. The trench width determines the length of the suspended devices, yielding a high-degree of reproducibility of this dimension from ribbon to ribbon. In order to show that the structures are suspended, all SEM images were performed with a tilt in the sample of 70°. Note that this tilt provokes that only the center of the image is totally focused and that dimensions in the vertical direction are apparently compressed by a factor cos(70).

Different ribbons (defined as primary ribbons) containing each one several suspended devices (defined as secondary ribbons) can be seen. Fig. 2(a) and (b), in particular, shows two magnified SEM images of the obtained suspended graphene. As it can be seen, the primary ribbons are remarkably straight, although they inevitably differ from one to another as a result of the exfoliation and transfer process. On the other hand, the secondary ribbons, i.e. the suspended devices, have very high shape regularity, with a constant width, *w*, and length, *l*. The obtained structures have a width between 0.2 and 1 μm. Each primary ribbon can contain from 2 to up to 50 secondary ribbons, paving the way to a systematic study of their properties, due to their high regularity. Fig. 2(c) gives a graphical idea of the primary ribbon density obtained by this method: more than 5 primary ribbons each one with more than 10 secondary components can be counted in an area of approximately $40 \times 70\ \mu m^2$. In this case, the 100 nm wide trenches have not been successfully patterned and only secondary ribbons defined by 300 nm and 600 nm trenches have been successfully suspended has it is shown by zoon-in SEM image of Fig. 2(d).

3.2. Raman spectroscopy

Raman spectroscopy has been successfully utilized as a convenient technique for identifying and counting graphene layers on different substrates [13–14]. It was shown that the evolution of the 2D-band Raman signatures with the addition of each extra layer of graphene can be used to accurately count the number of layers [13] together with the position of G peak, which up-shifts with the increasing $1/n$, where n is the number of graphene layers [15].

The quality and number of layers of the suspended graphene ribbons were evaluated by Micro-Raman spectroscopy using a Jobin-Yvon T64000 with a liquid N_2-cooled CCD detector and the 514 nm excitation wavelength at low power levels to avoid laser heating and subsequent degradation of PMMA and graphene. Fig. 3 shows the typical Raman spectrum of a suspended monolayer graphene with a sharp G band ($\sim$1584 cm^{-1}) and 2D band ($\sim$2690 cm^{-1}) and a low G/2D ratio. The single layer nature of the graphene ribbon is further confirmed by the full with at half maximum (FWHM) of the Lorentz fit of the 2D band being $\sim$30 cm^{-1}. The small D peak ($\sim$1350 cm^{-1}) intensity indicates that the graphene has low defect density. The peaks marked with a star (*) are originated in the PMMA layer [16] also excited with the incident laser radiation.