Large Area Extreme-UV Lithography of Graphene Oxide via Spatially Resolved Photoreduction


†Dipartimento di Fisica, Università dell’Aquila, Via Vetoio, 67100, L’Aquila, Italy
‡CNR-ISOF, Via Gobetti 101, 40129 Bologna, Italy
§Dipartimento di Fisica, Università dell’Aquila, g.c. LNGS-INFN, 67100, L’Aquila, Italy

ABSTRACT: The ability to pattern graphene over large areas with nanometer resolution is the current request for nanodevice fabrication at the industrial scale. Existing methods do not match high throughput with nanometer resolution. We propose a high-throughput resistless extreme-UV (EUV) photolithographic approach operating with sub-micrometer resolution on large area (~10 mm²) graphene oxide (GO) films via spatially resolved photoreduction. The efficiency of EUV photoreduction is tested with 46.9 nm coherent light produced by a table top capillary discharge plasma source. Irradiated samples are studied by X-ray photoemission spectroscopy (XPS) and micro-Raman Spectroscopy (μRS). XPS data show that 200 mJ/cm² EUV dose produces, onto pristine GO, a 6% increase of sp² carbon bonds and a 20% decrease of C–O bonds. μRS data demonstrate a photoreduction efficiency 2 orders of magnitude higher than the one reported in the literature for UV-assisted photoreduction. GO patterning is obtained modulating the EUV dose with a Lloyd’s interferometer. The lithographic features consist of GO stripes with modulated reduction degree. Such modulation is investigated and demonstrated by μRS on patterns with 2 μm periodicity.

INTRODUCTION

Graphene, the two-dimensional hexagonal allotrope of carbon isolated in 2004 by Geim and Novoselov, has rapidly achieved increasing consideration in materials science and condensed matter physics because of the huge number of potential applications allowed by its peculiar properties. Important branches of technology like electronics or optoelectronics, dominated for decades by silicon, are today opening the doors to graphene. The rising carbon-based technology is proving to be a valid alternative to the silicon-based one in an era of challenges like the extreme miniaturization of devices and eco-sustainability. The fabrication of graphene-based nanostructures has been demonstrated with several approaches. Conventional electron beam lithography (EBL) combined with plasma etching has been successfully used to fabricate carbon-based nanodots, nanorings, and nanoribbons from graphene sheets. Gate-defined graphene quantum dots have been isolated from EBL patterned nanoribbons. Graphene quantum dots have been obtained also by current assisted rupture of suspended graphene under proper cryogenic conditions. Graphene nanoribbons have been patterned by local anodic oxidation (LAO). Graphene nanoribbons have been derived with chemical ways, synthesized by chemical vapor deposition-(CVD), cut by crystallographic etching, patterned by LAO, fabricated through atomically resolved bottom-up approaches, or stretched out in different ways by chemical unzipping of carbon nanotubes.

Despite the excellent ability of scientists to fabricate isolated graphene-based nanostructures, the way these objects can be assembled into miniaturized electronic devices or even into more complex microcircuits is still a challenging issue. Many strategies have been proposed to accomplish this task, but all of them adopt local approaches that limit the number of assembled elements to few units. Graphene-based microcircuits have been recently realized on graphene oxide (GO) films via direct visible laser reduction. Nanopatterns of reduced GO (rGO) have been obtained also using atomic force microscopy (AFM) by tip-induced local thermal reduction or electrochemical reduction. AFM lithography has been used directly on graphene films to engrave nanopatterns via local hydrogenation/oxygenation by just controlling the tip bias. Atomically structured graphene features have been obtained both by electron beam lithography and scanning tunneling microscopy lithography. All these strategies are good choices for a fine control of shape and dimensions of nanostructures but not for large-scale processing, their throughput being intrinsically small.

Received: November 24, 2011
Revised: February 22, 2012
Published: February 29, 2012
The need of high-throughput processes is driving scientists toward solutions inspired by existing technologies. Dimiev et al. have recently demonstrated the possibility of fabricating a graphene-based device drawing inspiration from standard lithography; in their approach, the lithographic steps consist in the layer-by-layer etching of graphene—or graphene-like materials—selectively masked by predesigned zinc patterns; the correct sequence of steps gives the desired graphene pattern, analogously to what happens when a silicon wafer is processed in a standard lithographic stepper. Another possible approach—drawing inspiration from standard lithography as well—is to use light for photoinduced patterning of graphene-based layers. The effects of light have been widely studied for graphene and GO at various wavelengths. In particular, UV wavelengths—typically used in the processes of photolithography—are known to have a reducing effect on GO but most of the works report about bulk processes where GO sheets are suspended in liquid solutions containing nanoparticles catalysts, typically TiO$_2$, ZnO, or metals (Au, Pt, and Pd). Catalyst-free UV photoreduction of GO dispersed in aqueous solution has been demonstrated using intense UV light, which creates high temperature and reactive environment.

An example of UV-assisted photopatterning has been also reported demonstrating that micrometer size conductive patterns can be obtained on insulating GO. An original idea is to use extreme-UV (EUV) instead of UV light for GO photopatterning. EUV light is considered since long the natural candidate to go beyond the resolution limits imposed by UV radiation in standard photolithography (currently operating with silicon-based materials only). Once EUV is aimed to an effective photolithography of GO, one has to cope with two limitations, namely the occurrence of possible in plane breaking of carbon—carbon bonds (that introduces defects in the graphene layer) and also photothermal effects (that limit the lithographic spatial resolution). Indeed, GO photoreduction is available in a range of photon energies that covers the entire EUV range, i.e., beyond the threshold for photoreduction (3.2 eV) and below the energy threshold that causes breaking of the in-plane carbon—carbon bonds in single-layer exfoliated graphene (200–300 eV). Thus, the choice of EUV radiation of a few tens of electronvolts nicely fits into these two boundary energy limits. Moreover, the condition for the photopatterning resolution limit to scale with the diffraction limit (down to tens of nanometers or lower) is the absence of photothermal effects. Up to now, such effects have been explicitly exploited for visible laser-induced photopatterning, or they have been found, in any case, to play an important role in UV-assisted processes. Nonetheless, the loss of spatial resolution owed to such thermal effects can only be avoided by using small EUV radiation doses (namely, several orders of magnitude lower than those used by Zhang et al. and by Zhou et al.).

Here we propose a high-throughput EUV (26.4 eV) lithographic approach for large area (~10 mm$^2$) GO sub-micrometer scale photopatterning. Besides lying in the opportune range for GO photoreduction, the photon energy we adopt here for our purposes matches well the energy of the O 2s electronic states in the GO valence band, an ideal condition to improve the absorption of the EUV photons and to enhance the efficiency of the photoreduction process. GO photoreduction is studied by X-ray photoemission spectroscopy (XPS) and micro-Raman spectroscopy ($\mu$RS). The reduction process is catalyst-free and consists in a highly efficient dissociation of epoxy and hydroxy groups due to the direct action of the EUV photons. The values of irradiance used in our experiments are small enough (20 mW/cm$^2$, i.e., $10^9$–$10^{10}$ times smaller values than in refs 24 and 25) to be confident that photothermal effects are negligible. Patterns with micrometer and sub-micrometer sized features are obtained by interference...
lithography. The reduction degree of the micrometer sized features is studied by μRS, giving a direct evidence of a modulation of the local GO reduction. The possibility—here demonstrated—of using EUV light to pattern GO is a relevant upgrade for the graphene-based technology that can take advantage, in this way, from the entire know-how of the EUV-based technology.

**EXPERIMENTAL SECTION**

Large area (100s of μm²) GO sheets are prepared via a modified Hummers method, starting from graphite flakes of 500 μm maximum size. The resulting GO is dispersed in water and then spin-coated at 2000 rpm on 72 nm thick Al₂O₃/Si(100) previously sonicated in NH₄—OH solution (Figure 1). The thickness of the Al₂O₃ film is specific for best optical contrast of the deposited GO sheets. Deposition monolayers are identified by simple optical inspection on the basis of the calibration given in ref 43. The thickness of the observed monolayers is 1.1 ± 0.1 nm. A standard optical microscope (Olympus BH2-UMA) equipped with four different objectives (5X, 20X, 40X, and 100X Olympus objective) and a scanning electron microscope (SEM) (ZEISS-GEMINI LEO 1530) have been used to observe the surface of the samples. Optical images (20X magnification) of the as-deposited GO sheets are reported in Figure 1, at two different surface coverage conditions. The surface density of GO flakes is, in general, increased by multiple depositions. In our case, a double deposition is enough for an almost complete paving of the substrate surface, as shown in Figure 1d. An image of sample prepared by single deposition is reported in Figure 1c.

The EUV light source used to reduce GO is a compact table-top laser—almost unique in the world scenario—emitting at λ = 46.9 nm. The laser pulse (1.5 ns duration, 150 μJ energy) is produced by the single pass amplification of the 3p−3s transition in Ne-like Ar in an elongated plasma column created by a fast capillary discharge. Effects of the exposure of GO sheets to EUV light have been studied both by room temperature micro-Raman spectroscopy (μRS) and X-ray photoemission spectroscopy (XPS). In both cases the sample surface has been investigated both before and after EUV exposure. A LABRAM spectrometer (Horiba-Jobin Yvon, λ = 633 nm, 1 μm spatial resolution, and ~2 cm⁻¹ spectral resolution) equipped with a confocal optical microscope (100X MPLAN objective with 0.9 numerical aperture and 0.15 mm work distance) has been used for μRS, while a PHI 1257 spectrometer (monochromatic Al Kα source, hν = 1486.6 eV) has been used for XPS (base pressure 2 × 10⁻¹⁰ Torr). Samples have been exposed to EUV light under high-vacuum conditions (~10⁻¹³ Torr) and then investigated in air for μRS analysis or in ultrahigh vacuum (UHV) for XPS analysis.

Interference lithography has been performed using a simple Lloyd’s interferometer (illustrated in Figure 5a), exploiting the excellent coherence properties of the EUV laser source. The formation of periodic patterns is the outcome of the modulation of the EUV dose over the sample surface. No photoresists are used in the lithographic process. In the Lloyd’s configuration, half of the laser beam (~2 mm spot radius on the sample, Figure 1b) grazes the Lloyd’s mirror (0.5 nm rms Si reflecting surface) at an angle θ. The reflected half-beam overlaps the undeflected one forming an interference pattern over a ~10 mm² area with half-moon shape. The period p of the periodic pattern is easily tunable by varying the angle θ, p being defined by the simple relation \( p = \lambda / (2 \sin \theta) \). Using \( \lambda = 46.9 \) nm, the period can be scaled down to 23 nm.

**RESULTS AND DISCUSSION**

μRS spectra have been collected on monolayer GO both before and after EUV exposure (Figure 2). Samples have been exposed to a 200 mJ/cm² EUV dose, that is, the same dose hereinafter used for XPS analysis. Intensities are normalized to the G peak. The left-hand peak (D peak) is commonly related to the presence of defects while the right-hand peak (G peak) is characteristic of graphene. The ratio \( I_D / I_G \) between D and G peak intensities is related to the average size \( L_a \) of sp²-hybridized carbon domains (i.e., graphene-like domains) by the Tuinstra–Koenig equation. Here, \( I_D / I_G \) passes from 1.350 ± 0.005 (as-deposited GO) to 1.310 ± 0.005 (irradiated GO), corresponding to a 3% increase in \( L_a \) (that passes from 6.1 to 6.3 nm). Hence, the evolution of the Raman spectrum indicates that GO is reduced as a consequence of EUV laser exposure.

A systematic study of the properties of GO reduced by thermal annealing in UHV has been recently reported by our group, demonstrating the possibility of recovering almost completely the optical contrast of graphene at 670 °C. The data reported in ref 53 will be used here for a calibration of the GO properties in terms of the annealing temperature. According to this calibration, the above measured variation of \( I_D / I_G \) is found to correspond to a 60 ± 10 °C thermally induced reduction.

A dose-dependent μRS analysis has been performed to investigate the effects that higher doses have on monolayer GO. A plot of \( I_D / I_G \) as a function of the EUV dose is reported in Figure 3. As expected for a photoreduction process, the ratio...
$I_0/I_c$ regularly decreases as the EUV dose increases. At these regimes neither saturation nor degradation processes are observed. The slope obtained from a linear fit of the experimental data (dashed line) is $-3 \pm 2$ (J/cm$^2$)$^{-1}$, corresponding to a $2 \pm 1\%$ variation of $I_0/I_c$ per J/cm$^2$. This value of photoreduction efficiency is 2 orders of magnitude higher than the one measured in the case of UV-assisted photopatterning. Such a huge enhancement of the efficiency value of photoreduction efficiency is 2 orders of magnitude greater than the one measured in the case of UV-assisted photopatterning.

In particular, the decrease of the oxygen-related component of the XPS spectrum indicates that the oxygen atoms are the main responsible of the GO EUV light absorption, whose cross section is large enough to allow an efficient process of photoreduction. Due, in fact, to the resonance (at ~27 eV) of the EUV photons of our setup with the O 2s electrons, the photoabsorption at the oxygen atoms is enhanced with consequent break of the various C–O bonds. A quantitative estimate of the amount of oxygen atoms dissociating from GO sheets under the effect of the EUV light is obtained from the evolution of the areas of C–O and C$_{sp2}$ peaks. A 6% increase of sp$^2$ carbon bonds and a 20% decrease of C–O bonds are found. Such values correspond to a ~50 °C thermally induced reduction (in UHV)$^{53}$ in good agreement with the result obtained by µRS (60 ± 10 °C).

The demonstration of a high-efficiency photoreduction effect of EUV light on as-deposited monolayer GO suggests its application to photolithography. Here we report GO patterning via spatially resolved photoreduction. We demonstrate a simple periodic patterning modulating the EUV dose with a Lloyd’s interferometer (Figure 5a). No photoresists are used in the process. The patterns, as they are observed with the optical microscope, consist of alternated darker/lighter stripes (Figure 5a,b). The exposed monolayer GO sheets are deposited on 72 nm thick Al$_2$O$_3$/Si(100). Images of patterns with 2 μm and 500 nm periodicity are reported respectively in Figure 5b,c. Corresponding features are 1 μm and 250 nm sized, respectively. A detail of fringes is reported in both cases (bottom of each box). Folds of the single-layer GO sheets (spread out as a tablecloth on the substrate) can be easily distinguished. Patterns cover a wide area (~10 mm$^2$) wherein they preserve the same period and good contrast. The 250 nm sized features are less resolved than the 1 μm sized ones but they are still visible.

The micrometer scale patterns of Figure 5b have been used to investigate the reduction degree of the single periodic feature by µRS. A first evidence of reduction degree modulation is given by the modulation of the color contrast (dark and light stripes) exhibited by the EUV-exposed monolayer GO when observed at the optical microscope (Figure 6a,b). In particular, darker stripes are those with a higher reduction degree.$^{59}$ The width of the stripes (1 μm) matches well the lateral resolution of the visible laser equipping the Raman spectrometer. The measure has been repeated on several stripes to achieve statistical significance. Collected spectra (Figure 6c,d) are identical to the spectrum reported in Figure 2 for photoreduced monolayer GO but with slight variations in the D peak intensity (as in the case of Figure 2, spectra are normalized to the G peak intensity). The gap here observed is much smaller than in Figure 2 but it is still significant. $I_D/I_G$ passes from 1.315 ± 0.005 (lighter stripes) to 1.305 ± 0.005 (darker stripes). Because of a background superimposed to the dose modulation—and increasing with the dose itself—GO is reduced in both dark and light stripes.

**CONCLUSIONS**

In this work, we have reported the first demonstration of resistless EUV lithography on monolayer GO. In particular, we...
have demonstrated that supported GO (GO on 72 nm thick Al₂O₃/Si(100)) can be reduced with a high efficiency process by direct EUV light exposure and that single monolayers can be patterned over large areas (∼10 mm²) with sub-micrometer resolution via spatially resolved photoreduction. Despite the choice of a specific substrate (motivated by the need of enhancing the optical contrast of the patterned features on top of it), the results are of general validity. The technique has proved to be a promising candidate to fabricate integrated graphene-based nanocircuits because parallel, operating on large areas, and resistless. Given this proof of concept, the process can be very likely significantly improved with the use of high-performance sources like synchrotron or free electron laser.

Figure 5. (a) The Lloyd's interferometer used to pattern the GO flakes: detail of the patterning area (top) and schematic top view (bottom). In the Lloyd's configuration, half of the laser beam grazes the Lloyd's mirror at an angle θ and overlaps the undeflected half-beam to form the interference pattern. (b, c) SEM images of the patterned monolayer GO (white grids are enclosed in (c)). Patterns with 1 μm (b) and 250 nm (c) sized features have been realized.

Figure 6. (a, b) Optical observation of the features: 100X image (a) and detail (b). (c–e) Room temperature micro-Raman analysis: spectra have been collected on dark (c) and light (d) stripes (both normalized to the G peak intensity), as schematically illustrated in (e). (f) Difference between the two spectra (I_light − I_dark). Red and blue colors have been used to associate each spectrum to the selected stripe.

ASSOCIATED CONTENT

S Supporting Information
Quantitative estimation of the variation of sp² carbon bonds and C−O bonds due to photoreduction. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION
Corresponding Author
*E-mail: stefano.prezioso@aquila.infn.it.
Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was partly supported by the Istituto Nazionale di Fisica Nucleare (INFN) project XILOPHON. S. Prezioso acknowledges individual grant from CARISPAQ (Cassa di Risparmio Provincia dell’Aquila). Authors acknowledge M.


(50) This limit can be extended to even lower values if facilities like synchrotron or free electron laser are used.


