In this paper we report our recent studies on the fundamental physical/chemical properties of supported reduced Graphene Oxide (rGO) obtained either via standard thermal annealing or under extreme-UV (EUV) light exposure alongside with investigations on its possible technological applications. rGO has been studied by X-ray Photoelectron Spectroscopy (XPS), micro-Raman Spectroscopy ($\mu$RS), and Optical Microscopy. rGO reduction degree has been calibrated on the basis of its color contrast (CC) providing a handy tool to quantitatively determine the fraction of sp$^2$-hybridized carbon and the surface area ratio occupied by pure graphene puddles as GO is reduced [1].

Large area (100's μm$^2$) GO sheets have been prepared via a modified Hummers method [2] and deposited by spin coating on 72 nm thick Al$_2$O$_3$/Si(100) [3]. Thermal reduction has been performed in the range between room temperature and 670 °C (Fig. 1(a)). When going from pristine GO to 670 °C annealed GO, the CC passes from 0.4 ± 0.02 the one measured for graphene to ~ 1, the fraction of sp$^2$-hybridized carbon passes from 0.46 to 0.78, and the average size of pure graphene puddles passes from 6.0 nm to 8.0 nm at 400 - 500 °C (7.5 nm at 670 °C). EUV-assisted photoreduction has been performed with 46.9 nm coherent light produced by a table top capillary discharge plasma source almost unique in the world scenario. The energy of photons (26.4 eV) lies in the opportune range for GO photoreduction, i.e. beyond the minimum energy required for photoreduction (3.2 eV) [4] and below the energies that cause breaking of the in-plane carbon–carbon bonds in single-layer exfoliated graphene (200−300 eV) [5]. When exposed to 200 mJ/cm$^2$ dose, GO exhibits a 6% increase of sp$^2$-hybridized carbon and a 20% decrease of C−O bonds, corresponding – according to the CC-based calibration – to a 60 ± 10 °C thermally induced reduction (Fig. 1(b)) [6]. Photoreduction performed under these conditions has proved to be 2 orders of magnitude more efficient than the one measured in the case of UV-assisted photopatterning [7].

The original choice of using EUV instead of UV light to photo-reduce supported GO is not only advantageous in terms of reduction efficiency but it also allows to introduce the concept of EUV photolithography (today limited to the silicon technology only) for the processing of graphene-based materials. Here we demonstrate resistless sub-micrometer GO photo-patterning over large areas (~ 10 mm$^2$) [6], in line with the current request of nanometer level patterning on wafer-sized areas. Regular periodic patterns are obtained by interference lithography (Fig. 1(c)). The patterned features consist of GO stripes with modulated reduction degree. The darker stripes (as observed at the optical microscope) are those with the higher reduction degree (as measured by μRS on patterns with 2 μm periodicity), consistently with the contrast enhancement that is observed as a function of the reduction degree [8]. This result 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 in view of an eco-sustainable all-carbon technology.
References


Figures

Figure 1: (a) optical images of GO reduced at different temperatures. (b) C 1s XPS spectra (left) and Raman spectra (right) of GO before and after EUV exposure. (c) Schematic view of the Lloyd’s interferometer used to pattern the GO flakes (left) and SEM images of GO patterns with 1 μm and 250 nm sized features (right).