SYNTHESIS OF GRAPHENE FILMS ON COPPER SUBSTRATES BY CVD OF DIFFERENT PRECURSORS

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Chemical Vapor Deposition of graphene and few layer graphene (FLG) films is a promising technique for device fabrication since it allows to deposit large area graphene that can be transferred on nonspecific substrates [1,2]. In the literature it has been reported that the growth of graphene on metal surfaces can be affected by several factors, including the carbon solubility in the metal, its crystal structure and the thermodynamic and kinetic parameters [3].
Copper has been extensively used as growth substrate due to its very low carbon solubility (less than 0.001% At) that is thought to be responsible for the self-limiting precipitation growth and surface decomposition of carbon-containing molecules [1,3].
Among the large variety of precursors, hydrocarbons are the most widely used, while only a few papers report on the ethanol CVD [4,5], whose decomposition into "hydrocarbon" and "weak oxidizing" radicals at high temperature could help in graphene growth, as demonstrated for long and less defective carbon nanotubes [6].
In the present work, graphene films of the order of centimeters were grown on copper foil substrates by CVD using hydrogen/methane or hydrogen/argon/ethanol mixtures as gas precursors. The growth processes were performed at 1000°C both at atmospheric and low pressures. A system for the fast cooling of the sample, based on the fast extraction of the sample from the hot zone of the furnace, has been implemented allowing for rapid decrease of the sample temperature below 600°C in few seconds.
After the growth the graphene films were transferred to Si/SiO_2 (500 nm thermal oxide) substrates according to the following procedure: first the copper foil was etched in an acid media solution (fig.1a); the floating carbon film was then washed, and, while floating, it was caught and transferred to Si/SiO_2 substrate (fig.1b), taking advantage of its adherence to silicon oxide surface.
Samples grown under different conditions were analyzed by SEM, Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and AFM, with the aim to assess their characteristics and to refine the growth process.
The films consisted of FLG, whose number could be decreased by tuning the process parameters.
XPS analysis and SEM observations showed that copper oxide debris, resulting from the

metal oxidation during acid treatments, could contaminate the graphene films, pointing out the need of further chemical treatments before the transfer.
The SEM image reported in figure 2a shows a continuous graphene film with its typical wrinkles. Copper grain boundaries are also visible.
A Raman spectrum of graphene consists of three major features: the D ($\omega_D \sim 1350$ cm^{-1}), G ($\omega_G \sim 1586$ cm^{-1}) and 2D ($\omega_{2D} \sim 2686$ cm^{-1}) bands. The ratio between the intensities of the two latter bands and the width and profile of the 2D band are sensitive to the number of layers, whereas the intensity of the D band is related to disorder and defects in the graphene planes. In our samples, irrespective of the band width, the 2D band profile can be fitted with a single lorentzian peak, as it has been previously reported for CVD grown single graphene layer or FLG [7], or even turbostratic graphite [8]. However, as shown in Fig. 2b, for a sample grown by methane CVD, the FWHM of the 2D band is 31cm^{-1} and the intensity ratio I_{2D}/I_G is 1.4, approaching the typical values of single layer.

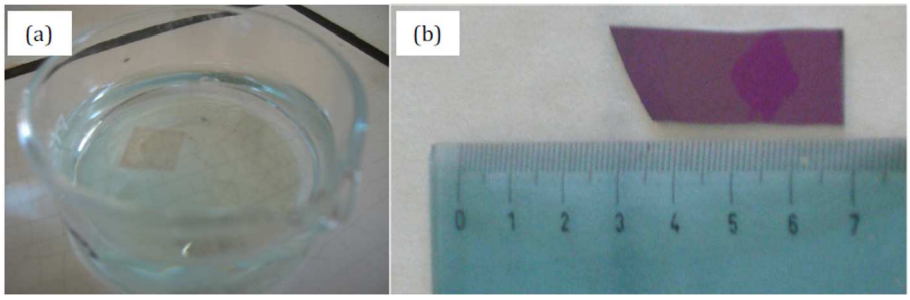

Figure 1: Etching of Cu foil by acid media solution (a) and graphene layers transferred onto Si/SiO_2 substrate (b).

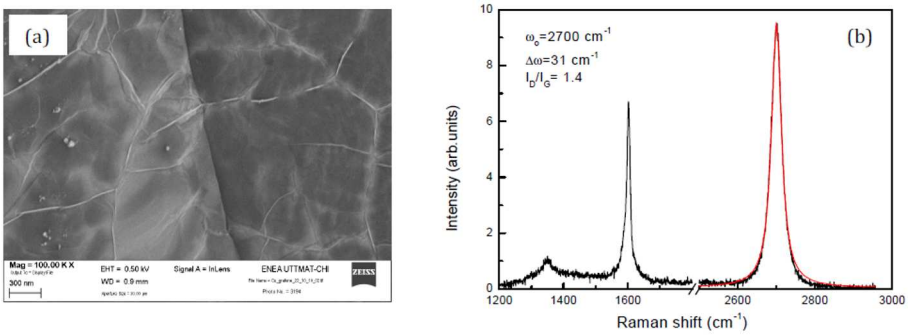

Figure 2: SEM image of the as synthesized graphene film on Cu substrate (a) and Raman spectrum with lorentzian fit of the 2D band of a graphene film transferred onto Si/SiO_2 substrate (b).

References

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