Graphene: different fabrication technologies for solid state devices

T. Polichetti[(1)], L. Lancellotti[(1)], E. Massera[(1)], M. L. Miglietta[(1)], F. Ricciardella[(1)], S. Romano[(1)], O. Tari[(2)], S. Gnanapragasam[(1)] and G. Di Francia[(1)]

R. Giorgi[(3)], T. Dikonimos[(3)], N. Lisi[(3)], E. Salernitano[(3)], S. Gagliardi[(3)], M. Falconieri[(3)]

[(1)] ENEA-UTTP-MDB Portici ENEA, p.le E. Fermi, 1, Portici (Naples), I-80055, Italy

[(2)] University of Naples "Federico II" Dept. Electronic Engineering, Via Claudio 21, 80125 – Naples, Italy

[(3)] ENEA-UTTMAT-SUP Casaccia ENEA, via Anguillarese 301, 00123 Roma, Italy

Corresponding author: tiziana.polichetti@enea.it

The ideal technique for fabricating graphene, i.e. a method able to produce a real single monolayer on a large area, is still far from being developed; up to now the existing techniques [1-9,12] involve both advantages and drawbacks and imply the achievement of a tradeoff for the application it is intended to make. For example, the mechanical exfoliation has a limit in the dimension of flakes, usually in the range of the microns; this kind of graphene, however, posses the best electrical and mechanical properties, appropriate for fundamental research purposes.
Herein we present the results related to the fabrication, characterization and applications performed under the topic "Graphene" in the two laboratories of ENEA Casaccia and ENEA Portici, where we have diversified the fabrication technology of graphene, based on specific requirements of the application to which it was intended.
At the Surface Technology laboratory of ENEA Casaccia the graphene growth by thermal CVD on metal substrates is being pursued: the effect of varying process parameters on the quality of the graphene film is being investigated, while aiming at obtaining large area, large single crystal domain, homogeneous and continuous films for the applications. The graphene film growth is performed in a hot wall CVD reactor consisting of a quartz tube equipped with a "home-built" system for the fast insertion and extraction of the growth samples as shown in Fig 1. The fast extraction of the sample from the hot zone rapid cooling of the samples, thus a better process control. A wet etching procedure for the transfer of the free floating graphene films from Cu to SiO_2/Si substrate is presently being adopted, without the use of a resist.
Various gas precursor and vapour mixtures can be used, such as methane and ethanol vapour, diluted in argon and hydrogen. Acetonitrile was also utilized with the aim to deposit N-doped graphene films.
The samples are routinely analysed by scanning electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy. Graphene films with area of the order of 9 cm^2, consisting of very few layer (1-2) regions with small inclusions of multilayered regions, are grown [9]. The testing of graphene as DSSC counter-electrode is presently under way.
As for the ENEA Portici laboratory, the activity is concentrated mainly on the basic research on sensor devices and solar cells.
Concerning the sensor application, the most of the scientific community is moving on the chemical exfoliation methods, since they are low cost, versatile and do not affect the sensing properties of the graphene. In our labs a simple approach to fabricate conductometric sensors based on chemical exfoliated natural graphite has been performed. The devices, tested upon sub-ppm concentrations of NO_2 in controlled environments, have shown the ability to detect this toxic gas at room temperature (see Fig. 3), with an estimated detection limit as low as 40 ppb [10], consistent with the best performances observed in the few-layers devices [11].
In regards to the use of the material in fundamental studies, as said above, the technique that retains the original properties of graphene is undoubtedly the mechanical exfoliation. In our laboratories we have developed a method that relies on the highly oriented pyrolitic graphite exfoliation by means of a thermo-curable elastomer, polydimethylsiloxane (PDMS), that allows to achieve lateral dimensions of flakes of tens of microns [12]. Samples prepared by this technique were employed to realize MOS graphene-based structures and, through capacitance-voltage characterization, the graphene workfunction, which is dependent on the number of layers and is one of the most important physical parameters used in the solar cell simulations, was experimentally determined. The workfunction values were employed in a theoretical study on the performance of graphene-on-semiconductor Schottky barrier solar cells (SBSC), and the theoretical efficiency was then estimated as function of the graphene number of the layers [13]. The results allow to make predictions about the potential of graphene-based solar cells; in particular best performances have been achieved for a 6 layer graphene based SBSC with an efficiency value up to 6.86 in the case of graphene on p-type germanium (see Tab.1).

References

[1] S. N. Yannopoulos, A. Siokou, N. K. Nasikas, V. Dracopoulos, F. Ravani, G. N. Papatheodorou, Adv. Funct. Mater, **22** (2012) 113.
[2] P. J. Wessely, F. Wessely, E. Birinci, B. Riedinger, U. Schwalke, arXiv:1112.4320v1
[3] C. Vallés, J. D. Núñez, A M. Benito, W. K., Carbon , **50**, (2012) 835
[4] W. Gannett, W. Regan, K. Watanabe, T. Taniguchi, M. F. Crommie A. Zettl, Appl. Phys. Lett., **98** (2011) 242105
[6] G. Lippert, J. Dabrowski, M. C. Lemme, C. M. Marcus, O. Seifarth, G. Lupina, Phys. Status Solidi B, **248** (2011), 2619
[7] C. T. Nottbohm, A. Turchanin, A. Beyer, R. Stosch, A. Golzhauser, arXiv:1105.5792v1
[8] Q. Yu, L. A. Jauregui, W. Wu, R. Colby, J. Tian, Z. Su, H. Cao, Z. Liu, D. Pandey, D. Wei, T. F. Chung, P. Peng, N. Guisinger, E. A. Stach, J. Bao, S.Pei, Y. P. Chen, Nature Materials **10** (2011) 443
[9] R. Giorgi, Th. Dikonimos, M. Falconieri, S. Gagliardi, N. Lisi,P. Morales, L. Pilloni and E. Salernitano Springer Series Carbon Nanostructures - Luca Ottaviano Vittorio Morandi Editors - GraphITA 2011 ISBN 978-3-642-20643-6 Springer Heidelberg New York Dordrecht London p.109
[10] T. Polichetti, E. Massera, M. L. Miglietta, I. Nasti, F. Ricciardella, S. Romano and G. Di Francia Springer Series Carbon Nanostructures - Luca Ottaviano Vittorio Morandi Editors - GraphITA 2011 ISBN 978-3-642-20643-6 Springer Heidelberg New York Dordrecht London, p.171
[11] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, , Nat. Mater., **6** (2007) 652
[12] F. Ricciardella I. Nasti, T. Polichetti, M. L. Miglietta, E. Massera, S. Romano and G. Di Francia.: Springer Series Carbon Nanostructures - Luca Ottaviano Vittorio Morandi Editors - GraphITA 2011 ISBN 978-3-642-20643-6 Springer Heidelberg New York Dordrecht London, p. 187
[13] L. Lancellotti , T. Polichetti, F. Ricciardella, O. Tari, S. Gnanapragasam and G. Di Francia, paper to be submitted.

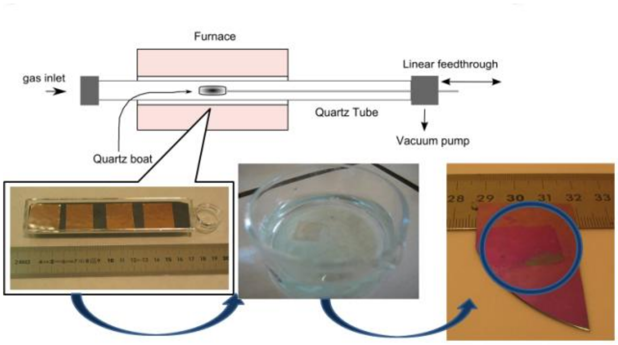

Figure 1 Scheme of the graphene growth apparatus and transfer

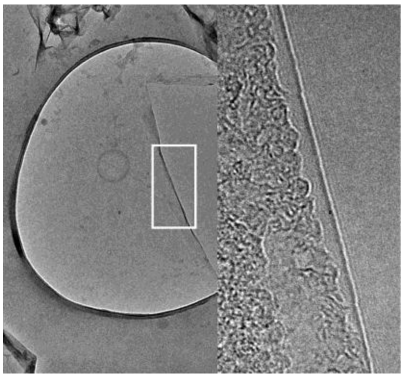

Figure 2. Tem micrograph of single layer graphene film grown in highly diluted methane in hydrogen

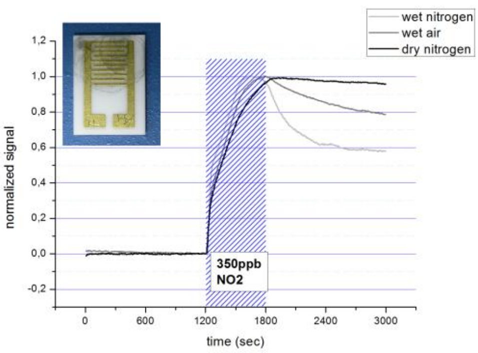

Figure 3: Normalized conductance response ((S-S0)/(Smax - S0)) kinetics upon exposure to 350 ppb of NO_2 in dry and wet carriers, with a flow of 500sccm at 22 °C. The device is DC biased at 1V. In the inset a device photograph of is reported.

Material	η(%)			
p-Si	0.11	0.232	0.98	1.58
n-Si	0.01	0.07	0.7	1.3
p-Ge	1.08	1.37	3.99	6.86
n-Ge	0.43	0.8	2.87	5.7
N	3	4	5	6

Table 1: efficiencies calculated simulating the electric behavior of graphene based SBSC devices with different combinations of semiconductor and number-of-layers of graphene, N.