



**Queensland University of Technology**  
Brisbane Australia

This is the author's version of a work that was submitted/accepted for publication in the following source:

Faggio, Giuliana, [Capasso, Andrea](#), Malara, Angela, Leoni, Enrico, Nigro, Maria Arcangela, Santangelo, Saveria, Messina, Giacomo, Dikonimos, Theodoros, Buonocore, Francesco, & Lisi, Nicola (2014)

Fast growth of polycrystalline graphene by chemical vapor deposition of ethanol on copper. In *9th Nanotechnology Materials and Devices Conference (NMDC 2014)*, 12-15 October 2014, Aci Castello, Italy.

This file was downloaded from: <http://eprints.qut.edu.au/87553/>

© Copyright 2014 IEEE

Personal use of this material is permitted. Permission from IEEE must be obtained for all other users, including reprinting/ republishing this material for advertising or promotional purposes, creating new collective works for resale or redistribution to servers or lists, or reuse of any copyrighted components of this work in other works.

**Notice:** *Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source:*

<http://doi.org/10.1109/NMDC.2014.6997424>

# Fast growth of polycrystalline graphene by chemical vapor deposition of ethanol on copper

Giuliana Faggio<sup>1,\*</sup>, Andrea Capasso<sup>2</sup>, Angela Malara<sup>1</sup>, Enrico Leoni<sup>2</sup>, Maria Arcangela Nigro<sup>1</sup>, Saveria Santangelo<sup>3</sup>, Giacomo Messina<sup>1</sup>, Theodoros Dikonimos<sup>2</sup>, Francesco Buonocore<sup>2</sup>, Nicola Lisi<sup>2</sup>

<sup>1</sup>DIIES - University “Mediterranea” of Reggio Calabria, Loc. Feo di Vito, I-89122, Reggio Calabria, Italy

<sup>2</sup>ENEA, Materials Technology Unit, Surface Technology Laboratory Casaccia Research Centre, Via Anguillarese 301, 00123, Rome, Italy

<sup>3</sup>DICEAM - University “Mediterranea” of Reggio Calabria, Loc. Feo di Vito, I-89122, Reggio Calabria, Italy

\*gfaggio@unirc.it (0965 875485)

**Abstract**— High conductive graphene films can be grown on metal foils by chemical vapor deposition (CVD) of both methane and ethanol. We here analyzed the use of ethanol, an economic precursor, which results also safer than commonly-used methane. A comprehensive range of process parameters were explored in order to obtain graphene films with optimal characteristics in view of their use in optoelectronics and photovoltaics. Commercially-available and electro-polished (EP) copper foils were used as substrates. By finely tuning the CVD conditions, depending on the surface treatments received by the copper substrate (which translate into different surface energies), such an enhanced nucleation brings about graphene films with different characteristics. On standard, unpolished copper substrates the film growth continues in time and finally leads to multilayer films with large domains of submicron size. On EP copper substrates instead, a mono-layer graphene made of nanocrystalline domains grows in a few seconds. de-activating the metal catalyst surface. Therefore, the growth on EP copper seems to be self-limiting because of its reduced catalytic effect. The growth from ethanol is in either case quicker than that from methane, with the formation of full graphene films in less than one minute.

As for the device properties, graphene with optimal properties as transparent conductive film were produced by CVD on standard copper with specific process conditions.

**Keywords**—graphene; chemical vapor deposition; ethanol; electropolished Cu.

## I. INTRODUCTION

Graphene films with high conductivity can be grown on metal foils by chemical vapor deposition (CVD) of various carbon feedstocks. Among all the approaches reported to date, this technique has caused great interest because of the low cost and the possibility to scale the production to large areas.

Although the use of a number of different carbon precursors and metal substrates was reported, the growth from methane on copper substrates has been the most intensively investigated [1, 2, Reina]. Upon the exposure of copper foils to high purity methane and hydrogen, high-quality and large-crystal uniform graphene films can be obtained [1]. Copper exhibit a low solubility for carbon atoms (<0.001 atom% at

1000 °C) thus restricting a self-limiting growth of graphene on top of the metal surface [1, 2]. Moreover, a number of studies showed that the morphology of Cu substrate influences the thickness uniformity of CVD-grown graphene [3, 4].

Alternative precursors were found in many other hydrocarbons, aliphatic alcohols [5] and organic molecules [6]. In particular, ethanol (C<sub>2</sub>H<sub>5</sub>OH) has been successfully used, being it an attractive choice for its safety, low cost, and easy handling [5, 7, 8]. Ethanol seems also to offer fast and efficient growth kinetics with the formation of fully-formed graphene films in just few seconds, probably because of more efficient dehydrogenation of the carbon precursor induced by oxygen atoms [9]. In this paper, we further explore the growth of graphene from ethanol, by comparing the graphene yield on unpolished (UN) and electropolished (EP) copper foils and focusing in particular on fast CVD.

## II. EXPERIMENTAL

### A. Sample Preparation

Electropolishing was performed with a home-built electrochemical cell on commercially-available copper foils (Cu-XLP/PHC 99,95), which were also used as received for comparison. This technique was successfully employed to eliminate impurity traces and smooth the surface of the foils, greatly reducing their roughness.

The growth on the different substrates was investigated by varying a comprehensive range of process parameters, such as reaction time and temperature, aiming at producing graphene films with optimal characteristics in view of their use in optoelectronic and photovoltaic applications. The detailed description of the CVD system can be found elsewhere [8]. It consisted of a hot-wall tube furnace where the samples can be rapidly inserted and extracted from the hot zone. Ethanol vapor was flown inside the quartz tube with Ar as carrier gas, at a pressure of few Pa. The growth was performed at the temperature of 1000-1070°C, and a hydrogen flow of 10 sccm was added as it has been found necessary to obtain thin and highly-crystalline graphene films [8]. An optimized CVD duration of 600 s was compared to quicker syntheses of 60 and

20 s [9]. After the CVD process, the films were transferred onto Si/SiO<sub>2</sub> (300nm) by using cyclododecane as support material during the copper etching in diluted nitric acid [10].

The cyclododecane transfer method was very recently proposed as an effective and facile means of processing CVD graphene.

### B. Sample Characterizations

Measurements of Micro Raman Spectroscopy, AFM, conductivity and transmittance were performed on the samples. Raman scattering measurements were carried out at room temperature with SA Ramanor U1000 double monochromator, equipped with an Olympus BX40 microscope for micro-Raman sampling and an electrically-cooled Hamamatsu R943-02 photomultiplier for photon-counting detection. The 514.5 nm (2.41 eV) line of an Ar<sup>+</sup> ion laser (Coherent Innova 70) was used to excite Raman scattering.

Using a x100 objective, the laser beam was focused to a diameter of approximately 1μm using a low laser power (below 1 mW). Three different locations were sampled on the transferred graphene films in order to discard possible spatial inhomogeneities. The Raman spectra were averaged and normalized to the G-band maximum intensity.

The sheet resistance of the films was measured by four-point probe method.

## III. RESULTS AND DISCUSSION

In Figure 1, AFM images of the Cu foil surface in the two cases are shown. The surface of the unpolished copper is very irregular, with an average roughness of 26.8 nm, but after the electropolishing this value reduces to an average of 5.8 nm.

Figure 2 shows the Raman spectra of graphene grown on UN copper and transferred onto Si/SiO<sub>2</sub> substrate. The main features are the G peak, centered at ~1584 cm<sup>-1</sup> and the 2D peak at ~2700 cm<sup>-1</sup>; D (~1350cm<sup>-1</sup>) and D' (~1620 cm<sup>-1</sup>) peaks are also observed, indicating the presence of defects in the graphitic lattice, such as disordered carbon, edges and wrinkles [11, 12].

It can be noticed that since the earliest stages of the growth process, the graphene film is multilayer ( $I_G/I_{2D} > 1$ ), but, as the time passes, the D band decreases and the G and 2D bands start progressively narrowing. This indicates that longer growth processes allow the lattice defects to heal, making the film increasingly more crystalline. It was, indeed, demonstrated in previous studies that the  $I_D/I_G$  ratios can reach considerably lower values when the growth time is extended up to 10 or 30 min [8, 13].

The Raman spectra of graphene grown on EP copper for varying times are reported in Figure 3 and some differences with the previous case are apparent. Since the beginning of the growth, a highly defective, monolayer graphene film seems to form ( $I_G/I_{2D} < 1$ ) and, although the D band again decreases with time, it never becomes as low as in case of unpolished copper.

As for the  $I_G/I_{2D}$  ratio, it progressively decreases with time while the bands narrow, demonstrating the formation of a single layer.

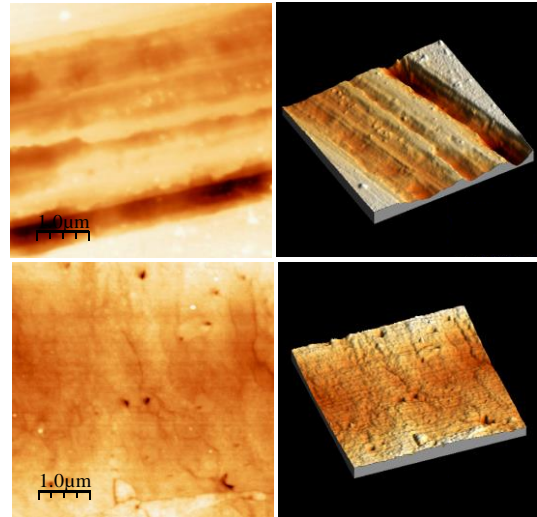


Fig. 1. AFM image of unpolished (top) and electropolished (bottom) Cu foil.

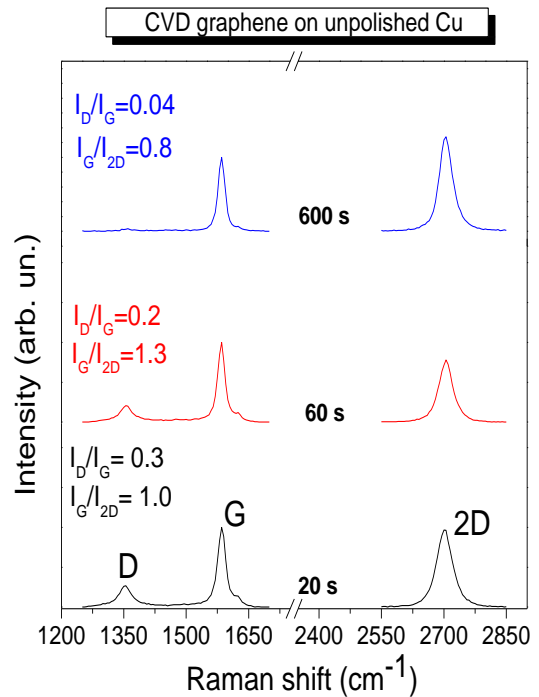


Fig. 2. Raman spectra of graphene grown on unpolished Cu foil for 600, 60 and 20 s.

The best film properties in terms of sheet resistance vs optical transmittance were obtained at 1070°C for 600 s, for both kinds of surfaces. On UN copper, a sheet resistance of ~500 Ω/sq with an optical transmittance around 92-94% at 550 nm was obtained, and the films were on average composed of

few layers (1-4). On EP copper instead, the films were always predominantly monolayer and showed a sheet resistance  $\geq 1000 \Omega/\text{sq}$  with a transmittance of 97.4%.

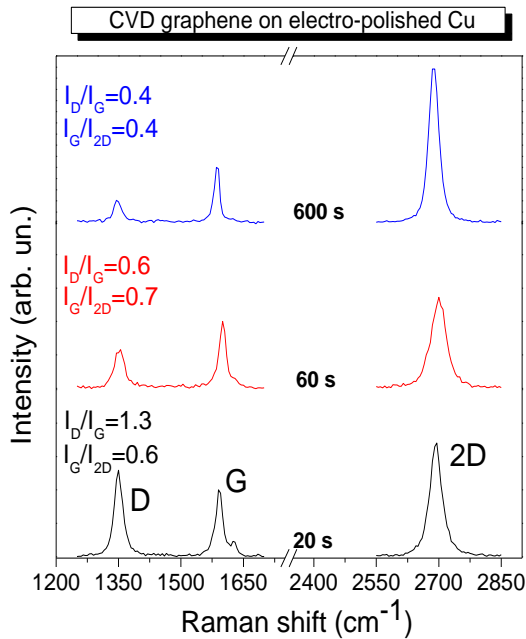


Fig. 3. Raman spectra of graphene grown at 1070°C on EP Cu foil for 600, 60 and 20 s.

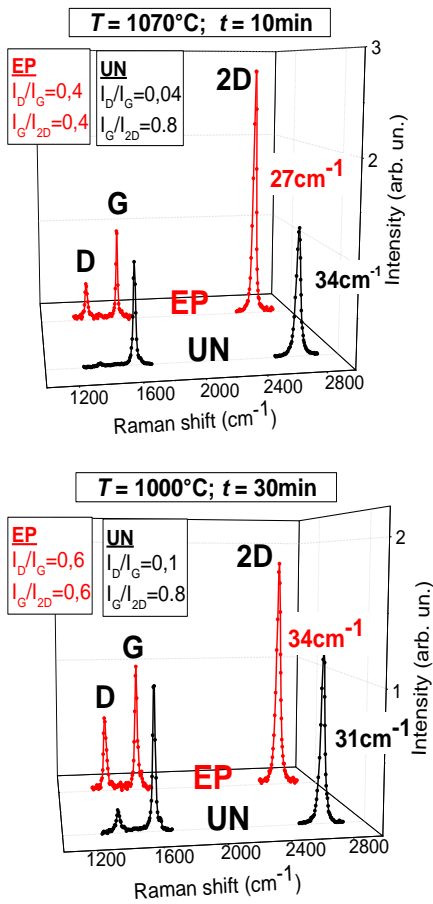


Figure 4. Raman spectra of graphene grown UN and EP Cu foils for (top) 10 min at 1070°C, (bottom) 30 min at 1000°C.

Figure 4 reports the Raman spectra of the graphene films with the highest quality obtained at high temperature in our experiments: 1070°C for 10 min with 10 sccm of H<sub>2</sub> and 1000°C for 30 min with 100 sccm of H<sub>2</sub>. The comparison highlights that, at both temperatures, on UN copper the graphene films result thicker ( $I_G/I_{2D}=0.8$ ) and with less defects ( $I_D/I_G=0.04-0.1$ ) than on EP copper. In the latter case, the films, though more defective ( $I_D/I_G=0.4-0.6$ ), show the typical Raman features of monolayer graphene, such as a  $I_G/I_{2D}$  of 0.4-0.6 and a symmetric 2D band shifted at lower wavenumber with a full-width at half-maximum of  $\sim 27-34\text{cm}^{-1}$ .

Table 1 reports the values of the graphene domain size ( $L_a$ ) evaluated from  $I_D/I_G$  integrated ratios for the various samples under examination [14]. With passing CVD time, the  $L_a$  of UN samples has a sevenfold increment, going from about 40 nm at 20 s to 280 nm at 600 s, proving that many lattice defects were healed. In the same time span, the  $L_a$  of EP samples has only a threefold increment and remains overall small, going from about 10 nm to 30 nm.

TABLE I. Graphene  $L_a$ .

t (s)	UN (nm)	EP (nm)
600	280	30
60	45	21
20	39	11

It was shown that  $I_D/I_G$  intensity ratio can be used experimentally to get information on the nature of defects in graphene [15]. The authors found that the  $I_D/I_G$  ratio is maximum ( $\sim 13$ ) for defects associated with  $sp^3$  hybridization, it decreases for vacancy-like defects ( $\sim 7$ ) and reaches a minimum for boundary-like defects ( $\sim 3.5$ ). In our Raman spectra the values of  $I_D/I_G$ , when measurable, are in the range 3-10, indicating that vacancy-like and boundary-like defects are mostly present.

On unpolished copper substrates, the film growth is fostered by defects and edges present on the copper surface (acting as nucleation sites) and continues in time, ultimately leading to few-layer graphene with turbostratic stacking-order and large domains (submicron size), as observed for 30-min CVD [8].

The topmost layers will be subject to a slower growth and weaker interaction with the copper substrate than those underlying; in this case, the growing domains will have the chance to extend unperturbedly and finally coalesce, reaching a superior degree of crystallinity. By contrast, on the flat surface of EP copper substrates a monolayer graphene can form in just a few seconds de-activating the catalytic activity of the metal surface. The growth is then limited to a monolayer, also because no additional nucleation centers stimulate the formation of secondary layers [16, 17]. The EP graphene is also made of small grains (which form in matter of seconds), but they do not seem to benefit much of the

increasing growth time, retaining a high concentration boundary-like defects. This might be caused by the low mobility of the adsorbed carbon clusters that nucleate very rapidly and in large number on the copper surface, “freezing” into a small-grain film.

#### IV. CONCLUSIONS

In conclusion, in our ethanol-CVD experiments, when electropolished copper foils are used as substrates, the resulting graphene is a monolayer with small grains, probably in the nanometric range. By contrast, on unpolished foils, the growth of a few-layer film of good crystalline quality can be expected. Due to the rapid growth kinetics associated with the use of ethanol as carbon precursor, the effect of the processing undergone by the substrate seems to have a dominant effect on the growth output, regardless of the variation of CVD parameters.

#### REFERENCES

- [1] X. S. Li, et al., “Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils”, *Science*, 324, pp. 1312-1314, 2009.
- [2] S. Bhaviripudi, X Jia, M S Dresselhaus, J Kong., “Role of kinetic factors in chemical vapor deposition synthesis of uniform large area graphene using copper catalyst”, *Nano Lett.*, 10, pp. 4128-4133, 2010.
- [3] A. Reina, et al., “Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition”, *Nano Lett.*, 9, pp.30-35, 2009.
- [4] Z. Luo, et al., “Effect of Substrate Roughness and Feedstock Concentration on Growth of Wafer-Scale Graphene at Atmospheric Pressure”, *Chem. of Mater.*, 23, pp. 1441-1447, 2011.
- [5] B. Zhang, et al., “Low-Temperature Chemical Vapor Deposition Growth of Graphene from Toluene on Electropolished Copper Foils”, *ACS Nano*, 6, pp. 2471-2476, 2012.
- [6] A. Guermoune, et al, “Chemical vapor deposition synthesis of graphene on copper with methanol, ethanol, and propanol precursors”, *Carbon*, 49, pp. 4204-4210, 2011.
- [7] Z. Li, et al., “Low-Temperature Growth of Graphene by Chemical Vapor Deposition Using Solid and Liquid Carbon Sources”, *ACS Nano*, 5, pp. 3385-3390, 2011.
- [8] X. Dong, et al., “Growth of large-sized graphene thin-films by liquid precursor-based chemical vapor deposition under atmospheric pressure”, *Carbon*, 49, pp. 3672–3678, 2011.
- [9] G. Faggio, et al., “High-Temperature Growth of Graphene Films on Copper Foils by Ethanol Chemical Vapor Deposition”, *J. Phys. Chem. C*, 117, pp. 21569–21576, 2013.
- [10] N. Lisi, et al., “Rapid and highly efficient growth of graphene on copper by chemical vapor deposition of ethanol”, *Thin Solid Films*, DOI: 10.1016/j.tsf.2014.09.040.
- [11] A. Capasso, et al., “Cyclododecane as support material for clean and facile transfer of large-area few-layer graphene”, *Appl. Phys. Lett.*, 105, 11310, 2014.
- [12] A.C. Ferrari, “Raman spectroscopy of graphene and graphite: disorder, electron-phonon coupling, doping and nonadiabatic effects,” *Sol. State Comm.*, 143, pp. 47-57, 2007.
- [13] M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio and R. Saito, “Studying disorder in graphite-based systems by Raman spectroscopy”, *Phys. Chem. Chem. Phys.*, 9, pp. 1276-1291, 2007.
- [14] S. Santangelo, et al., “Taguchi optimized synthesis of graphene films by copper catalyzed ethanol decomposition”, *Diam. Relat. Mater.*, pp. 73-78, 2014.
- [15] L. Cançado, et al., “General equation for the determination of the crystallite size  $L_a$  of nanographite by Raman spectroscopy”, *Appl. Phys. Lett.*, 88, pp. 163106, 2006.
- [16] A. Eckmann, et al., “Probing the Nature of Defects in Graphene by Raman Spectroscopy”, *NanoLetters*, 12, pp. 3925-3930, 2012.
- [17] R.K. Paul, et al., “The production of oxygenated polycrystalline graphene by one-step ethanol-chemical vapor deposition”, *Carbon*, 49, pp. 3789–3795, 2011.
- [18] P. Zhao, et al., “Self-Limiting Chemical Vapor Deposition Growth of Monolayer Graphene from Ethanol”, *J. Phys. Chem. C*, 117, pp. 10755–10763, 2013.