Graphene: large area synthesis by Chemical Vapor Deposition

The synthesis of graphene by Chemical Vapor Deposition (CVD) process is one of the most promising way for device applications since it allows producing large area films on suitable substrates. In this work graphene films of about 1cm^2 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 was implemented, allowing for a rapid decrease of the sample temperature below 600 °C in few seconds. Samples grown under different conditions were analyzed by SEM, Raman spectroscopy and XPS with the aim to assess their characteristics and to refine the growth process. Under the optimized conditions continuous films consisting of very few graphene layers (<5) were grown and transferred to SiO$_2$/Si substrates after Cu dissolution

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Grafene: sintesi su larga area mediante Deposizione Chimica da fase Vapore

Il processo di Deposizione Chimica da fase Vapore (CVD) è uno dei metodi più promettenti per la crescita di film di grafene in vista delle applicazioni in dispositivi, in quanto permette di ottenere campioni di grande area. In questo lavoro viene descritto il processo utilizzato per la sintesi di film di grafene di circa 1 cm^2, cresciuti su substrati costituiti da sottili fogli di rame, utilizzando miscele di idrogeno/metano o idrogeno/argon/etanolo come precursori gassosi. Le crescite sono state eseguite a 1000 °C variando la pressione. Il reattore è dotato di un sistema per il raffreddamento rapido dei campioni, basato sull'estrazione del campione dalla zona calda del forno, che permette di ridurre in pochi secondi la temperatura sotto i 600 °C. I campioni cresciuti variando i parametri di processo sono stati analizzati con diverse tecniche di caratterizzazione: SEM, Spettroscopia Raman e XPS. I film cresciuti nelle condizioni ottimali, trasferiti successivamente su substrati di SiO$_2$/Si dopo la dissoluzione del Cu, risultano continui sull'intera area e costituiti da pochissimi (<5) strati di grafene

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Introduction

Graphene, a single layer of carbon atoms arranged in a hexagonal network, is a 2D material with outstanding physical properties. The successful isolation of graphene [1] has drawn great interest for experimental investigations and has paved the way to a wide range of potential applications. Electronic and opto-electronic devices incorporating graphene as an active layer, such as high frequency transistors, solar cells, logic devices and interconnects in CMOS devices have been reported as proof of concept experiments. Recently nitrogen-doped graphene has been also studied as active material for ultracapacitors [2] and fuel cells [3]. The ability to create a device is facilitated by the availability of large-area graphene. Mechanical exfoliation of graphene from bulk graphite has enabled fundamental investigations on the physical properties of graphene; however, by using this technique it has not yet been possible to make large area graphene since the technique is not scalable.

Recently, considerable research efforts were spent on the synthesis of large area graphene by using different methods. Some of the most prominent methods include chemical modification of graphite, desorption of Si from either the Si plane or C plane of SiC substrates and catalyst-assisted synthesis in a chemical vapor deposition (CVD) reactor.

In this process, carbon-bearing gaseous species react at high temperatures (900-1100 °C) in the presence of a metal catalyst, which serves both in the decomposition of the carbon species and in the nucleation of the graphene lattice. The mechanism of graphene growth on metals is presumably influenced by several factors, including the carbon solubility limit in the metal, its crystal structure, lattice parameters and thermodynamic parameters such as the temperature and pressure of the system. In the case of intermediate-high solubility (0.1 atom %) metals, such as Co and Ni, graphene synthesis is thought to proceed via a combination of carbon atoms diffusion into the metal at the growth temperature and carbon atoms segregation from bulk to the metal surface on cooling after CVD process. In the case of very low carbon solubility met-

als (0.001 atomic %), such as Cu, the synthesis of graphene is on the other hand a process limited to the surface of the catalyst. The growth of graphene monolayers on single crystal transition metals such as Co [4], Pt [5], Ir [6.] Ru [7] and Ni [8] under ultra-high vacuum conditions is widely reported in literature. It is worth noting that single crystal substrates are desirable to grow defect-free graphene films, but in practice for large scale applications less expensive polycrystalline substrates must be used.

Polycrystalline nickel, as thin film, is one of the most commonly used substrate for metal assisted CVD graphene growth. Large area films growth has been reported [9] but the high carbon solubility and small grain size of this metal seem to limit the single layer defect-free growth.

Large area graphene synthesis using Cu catalyst has received widespread attention since it was first reported in 2009 [10-11]. Compared to other metal substrates, copper, besides having a very low carbon solubility, when annealed at temperature close to its melting point, experiences grain size growth needed for the achievement of large uniform graphene domains. Moreover copper has the advantage to be flexible when in foil of low thickness and for this reason apt to be processed with roll-to-roll technology[12].

Braviripudi et al [13] have demonstrated that the kinetics of graphene growth in a CVD process plays a critical role in the uniformity of large area graphene using Cu catalyst. Although the thermodynamics of the synthesis system remains the same, whether the process is performed at atmospheric pressure, low pressure (0.1-1 Torr), or under ultra-high vacuum conditions (10^{-4}-10^{-6} Torr), the kinetics of the growth phenomenon are different, leading to a variation in the uniformity of the graphene over large areas. Growing graphene large-area continuous films, with controlled number of layers, homogeneous and defect-free is still a challenge for researchers in view of numerous applications, ranging from electronics to new generation solar cells and organic lighting, where there is the need to develop transparent conductive electrodes alternative to the expensive indium thin oxide [14-15].

In our laboratory we have optimized the graphene

growth by thermal CVD on copper substrates by varying process parameters such as precursors mixture, gas flow rate, growth temperature, pressure and duration of the growth stage. Feedback on the quality of the samples was routinely obtained by scanning electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy. Graphene films with area of the order of 1 cm^2, consisting of very few layer regions with small inclusions of multilayered regions, have been grown. A procedure for transferring the graphene film from Cu to 500nm SiO$_2$/Si substrate has been also developed.

Experimental

Copper foils (PHC SE-Cu58) 25μm thick were used as growth substrate provided from Schlenk Metallfolien Gmbh.

The thermal CVD reactor consists of a quartz tube of 25 mm diameter placed horizontally into an oven (Fig.1). The gas precursors are admitted from one side with flows controlled by digitally-controlled flow meters while the pressure is regulated by the pump placed at the other end of the tube. A system for a fast extraction of the sample has been implemented for fast cooling that is needed to stop the growth of further graphene layers and for the additional possibility of processing and extracting several samples during a single heating cycle of the reactor. Fast cooling also prevents carbon segregation occurring on substrates with high carbon solubility at high temperature, even when the gaseous precursor has been switched off.

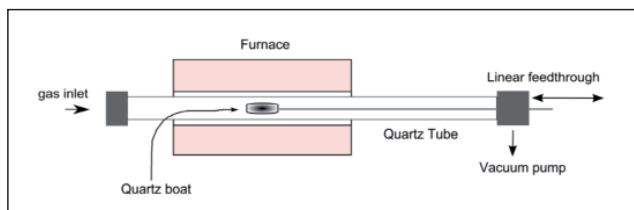Hydrogen/methane or hydrogen/argon/ethanol mixtures have been used for the synthesis. The growth process is illustrated in fig. 2: first the oven is heated in hydrogen/argon atmosphere, then the copper substrates are introduced into the hot zone and thus rapidly heated up to the process temperature, which was varied between 950 and 1050 °C. After a defined annealing time, the gas precursors mixture is introduced and the growth proceeds for the desired time. Then the gaseous carbon source is switched off and the sample is rapidly removed from the hot zone and cooled down at room temperature under inert gas. Table 1 shows the utilized process parameters.

Graphene coated copper substrates are available for a first observation with the Scanning Electron Microscopy (SEM). Then the graphene films are etched off from the substrate by dissolving the metal in aqueous solution of HNO$_3$. The resulting floating sheets, af-
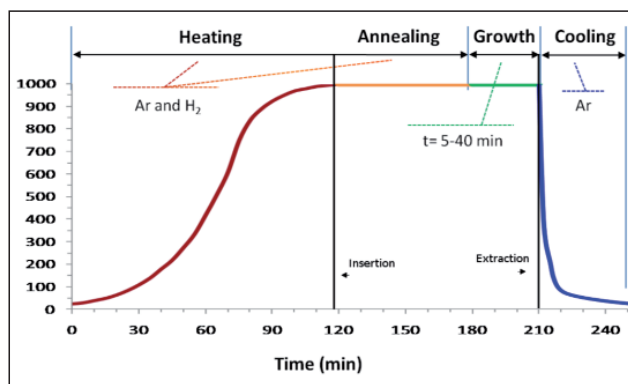
FIGURE 2 Grafene growth process
Source: ENEA

		Methane	Ethanol
Heating/Annealing	P	220 mtorr - 760 torr	4-750 torr
	Ar	0-200 sccm	15-60 sccm
	H$_2$	3-100 sccm	2-4 sccm
Growth	P	170 mtorr – 760 torr	4-750 torr
	Ar	0-200 sccm	-
	H$_2$	2-100 sccm	0-4 sccm
	CH$_4$	1-3 sccm	-
	C$_2$H$_5$OH	-	15-60 sccm
Cooling	P	760 torr	760 torr

FIGURE 1 Scheme of the CVD reactor
Source: ENEA

TABLE 1 Process parameters
Source: ENEA

ter washing in distilled water in order to remove contaminating particles deriving from copper dissolution, are transferred to 500nm SiO_2/Si substrates taking advantage of the strong adherence of graphene to the oxide surface, and ready for further characterization. Graphene films are characterized by SEM, Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). SEM observations were performed by a Field Emission Gun (FEG)-SEM (LEO1530) equipped with an in-lens secondary electrons detector; Raman spectra were acquired by a home-made Raman microscope, equipped with TRIAX 550 monochromator and a CCD detector and 532 nm excitation laser; XPS analysis were performed by a V.G. ESCALAB MKII, equipped with twin Al/Mg anode.

Results

Graphene films were grown on copper foils by CVD of carbon using two different precursors: methane and ethanol. According to Li et al [10], the thickness of Cu foils was not expected to influence the graphene growth; they have demonstrated in fact that Cu foils of varying thickness yielded similar graphene structure, showing that on copper graphene is growing by a surface-catalyzed process rather than a precipitation process, as reported by others for Ni [9, 16]. In order to increase the grain size of the substrate, samples underwent an annealing treatment before the graphene growth.

Two steps of the graphene transfer from Cu to SiO_2/Si substrate are illustrated in fig. 3, where the floating film during copper dissolution and the film adhering on the new substrate are shown in panel a and b respectively.

The transfer procedure from Cu foil to SiO_2/Si substrate was optimized evaluating, by XPS analysis, the occurrence of undesired film contaminations, e.g. as shown in fig. 4, where a small Cu signal due to residual nanoparticles, also seen by SEM, was detected besides the C, O and Si peaks.

Raman spectroscopy plays an important role in the characterization of graphitic materials. The Raman spectrum of graphene consists of three major fea-
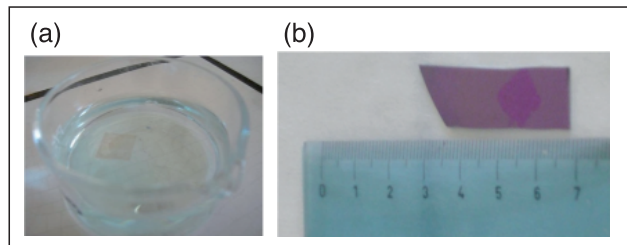

FIGURE 3 *a) graphene film floating during copper substrate dissolution, b) graphene film transferred on SiO_2/Si substrate*
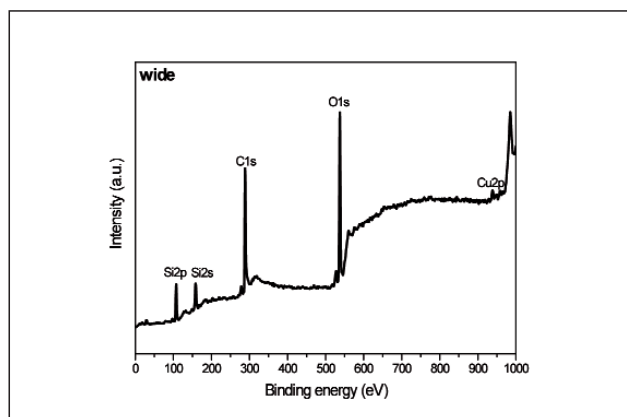*Source: ENEA*

FIGURE 4 XPS spectrum of a graphene film after the transfer on SiO_2/Si substrate
Source: ENEA

tures: D ($_D$~1350 cm^{-1}), G ($_G$~1586 cm^{-1}) and 2D ($_{2D}$~2686 cm^{-1}) bands. The G band is associated with the doubly degenerate (iTO and LO) phonon mode (E_{2g} symmetry) at the Brillouin zone center and it is the only band coming from a normal first order Raman scattering process in graphene. On the other hand, the 2D and D-bands originate from a second-order process, involving two iTO phonons near the K point for the 2D band or one iTO phonon and one defect in the case of the D-band. While the D band rises from structural defects in the *a-b* plane, the 2D band is allowed in the second order Raman spectra of graphene without any kind of disorder or defects. The intensity, the width and the profile of the 2D band are sensitive to the number of layers and to their stacking order

[17], whereas the intensity of the D band is related to disorder and defects in the graphene planes [18-19]. The monolayer graphene obtained by graphite exfoliation exhibits the following Raman features: 2D line width 24 cm^{-1} and I_G/I_{2D} ratio 0.25. As the number of layers increases, the 2D band profile becomes asymmetric and splits into more components and also the I_G/I_{2D} ratio increases. For more than 5 layers the spectra can be hardly distinguished from that of graphite. In turbostratic graphite (where the stacking of the layers is rotationally random with respect to one another along the *c* axis), the 2D band is a single lorentzian profile as in a monolayer graphene, but with a larger line width.

First we discuss the results obtained with methane. Initially samples were grown at temperatures up to 1000°C using a mixture of 25 sccm CH_4, 100 sccm H_2 and 200 sccm Ar, at 760 Torr. According to [13], under high methane concentration and high pressure the graphene growth on Cu was not a self-limiting process, as expected in the presence of a very low carbon solubility, and a multilayered film was obtained (sample GCu3). This is shown by the line width of the 2D Raman band reported in fig. 5, where Raman features of three different samples, transferred to oxidized silicon substrates, are reported. By decreasing the pressure down to 440 mTorr and the CH_4 flow rate to 3 sccm, a significant reduction of the film thickness
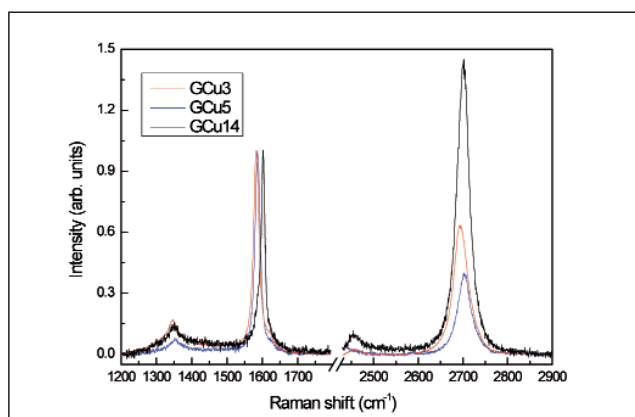
was obtained (sample GCu5): even though far from the typical monolayer graphene features, the 2D peak full-width-half-maximum (FWHM) was strongly reduced and the I_G/I_{2D} was also improved. Then the growth time was varied between 30 and 5 minutes. As the growth time decreased the graphene films quality improved, revealing a FWHM of 31 cm^1 and a I_G/I_{2D} of 0.7 for the shortest duration (sample GCu14 in fig.5). At the same time, a low intensity of the disorder-induced D band was observed, with $I_D/I_G = 0.15$ indicating that the amount of structural defects in the *a-b* plane was limited and the crystallinity high.

Ethanol has been widely reported as a gas precursor for single walled carbon nanotubes [20], much less extensively for graphene. Miyasaka et al [21, 22] have demonstrated graphene layers formation on Ni substrate with this precursor. Here graphene films were grown by using a mixture of argon and ethanol on copper foil, for sake of comparison with the CH_4 grown films. Samples grown at 1000 °C, at atmospheric pressure, with 60 sccm argon/ethanol mixture and for 30', resulted into a multilayered structure with a corrugated morphology, as shown in fig 6.

By lowering the pressure to 4 Torr, a remarkable film structure change was observed; the morphology features and Raman spectra are comparable with those of the best sample grown from CH_4. Further decrease of the ethanol concentration and growth time apparently did not result in different features. Figure 7 shows a SEM image of graphene grown from methane on a copper substrate where a grain boundary is clearly visible. The dimension of Cu grains is controlled by the annealing process performed before the graphene growth. The image shows the presence of graphene "wrinkles". The wrinkles, associated with the thermal expansion coefficient difference between Cu and graphene, are also found to cross Cu grain boundaries, suggesting that the graphene film develops continuously.

Samples grown from ethanol (Fig. 8) shows the presence of non-uniform dark regions occurring on an underlying pale grey background, where Cu surface steps, due to the reconstruction of the surface substrate under high temperature, are also visible.
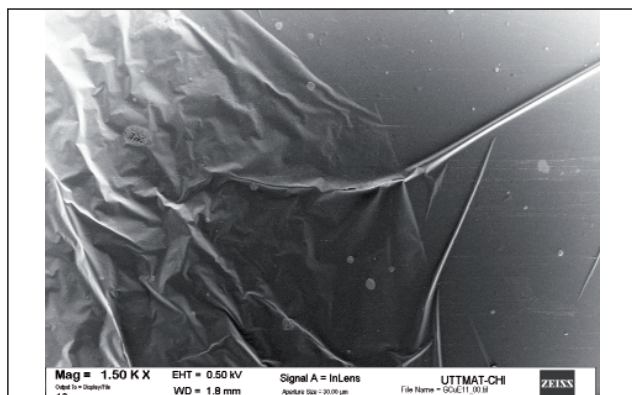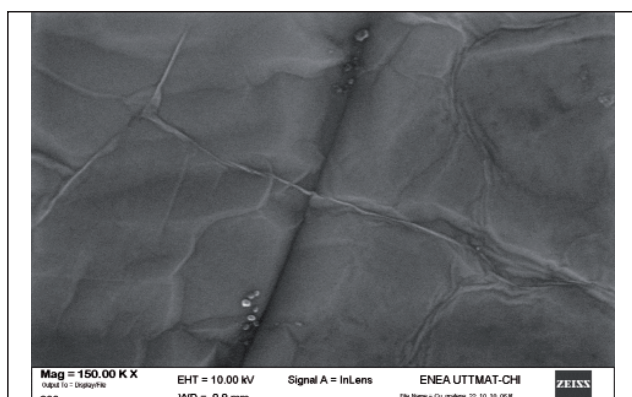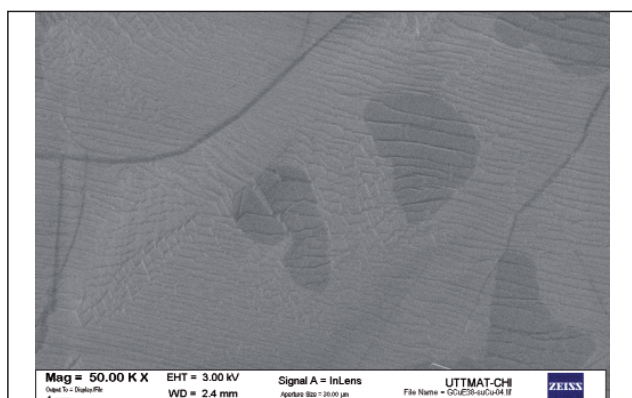

FIGURE 5 Raman spectra of samples GCu3, GCu5 and GCu14
Source: ENEA

The number of graphene layers determines the regions with different color: the more the film is thin, the more the color is bright. The percentage of the dark regions is influenced by several factors, also including growth process parameters such as carbon content and pressure, but mainly referable to the substrate structure. Grain orientation, boundaries, impurities and defects of the substrate, in fact, are reflected on the growing graphene, resulting in non-uniformity and non-homogeneity of the large area films especially.

The Raman analysis is averaged on an area of about ten microns, therefore the observed features could refer to regions with a different number of layers. Nevertheless, our best films exhibited a sharp 2D line with single lorentzian profile and width ranging from 31 to 37 cm^{-1}. This is consistent with non-interacting graphene planes, as reported for CVD-derived few layers graphene [9], where the long order in the c direction is lacking, unlike the exfoliated HOPG layers, where single-layer can be differentiated from bilayer and trilayer graphene by the shape of the 2D band. For CVD-derived graphene, 2D linewidth values around 33 cm^{-1} are reported as hallmark of less than 5 layers. Moreover by sampling different regions of the films, different values of the I_G/I_{2D} ratio were found. The best value of 0.7 is also consistent with the thickness of less than 5 layers. The high quality and crystallinity of the films was also evidenced by the low intensity of the D band, with $0.1 < I_D/I_G < 0.3$. The domain size L_a was also calculated by using the relation proposed by Cançado [23]: $L_a[nm] = (2.4 \times 10^{-10}) \lambda_{laser}^4 (I_D/I_G)^{-1}$, obtaining values ranging between 70 and 130 nm.

Conclusions

In summary this work shows that films consisting of less than 5 graphene layers have been grown by CVD both from methane and ethanol as precursors. The use of copper substrates has allowed growing large area continuous films (1 cm^2); a wet procedure was followed for transferring the graphene films onto SiO_2/Si substrates more suitable for the characterization. Pressure and growth time have been found the main

process parameters affecting the thickness and the quality of the graphene films. The films exhibited high *a-b* plane crystallinity, but a certain thickness non-homogeneity occurred, due to multilayered regions overlapping few layer-regions. A factor influencing the film homogeneity and uniformity has been recognized in the substrate features. Future work will be focused on the optimization of substrate treatments, with the aim to achieve more uniform large area single-layer graphene films.

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