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Characterization of graphene grown on copper foil by chemical vapor deposition (CVD) at ambient pressure conditions

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Abstract

In the aim to get high quality graphene films, with large domains and free from impurities, minimizing also the manufacturing costs, we investigate the graphene grown on copper (Cu) foil by chemical vapor deposition at ambient pressure conditions, by using methane (CH₄) as carbon source, diluted in a suitable mixture of argon (Ar) and hydrogen (H₂). Several graphene samples were synthesized, for variable exposure times to hydrocarbon precursor, in the range from 1 min to 1 hr. The quality of the graphene films and their structural, morphological, and electronic properties were evaluated by micro-Raman spectroscopy and other techniques, including, scanning tunneling microscopy, atomic force microscopy, and scanning electronic microscopy. In particular, samples obtained with shorter growth time (less than 10 min) exhibit a non-uniform coverage of the Cu surface, whereas those synthesized with exposure time between 10 and 30 min show a prevalence of well-ordered monolayer graphene domains. For longer deposition, the amount of disordered domains increases, as revealed by Raman analysis, and the resulting film shows a nonself-limiting growth behavior for chemical vapor deposition at atmospheric conditions. In addition, we observed 2 kinds of monolayer graphene, in terms of coupling with the Cu surface, for the samples synthesized between 10 and 30 min. To the best of our knowledge, “coupled” and “decoupled” graphene regions have never been reported at the same time on Cu surface. Furthermore, a Raman statistical analysis has been performed on the G and 2D bands measured in both the kinds of regions, gaining evidence of a bimodal behavior for the graphene spots, corresponding to “coupled” and “decoupled” configurations. This difference, which is appreciable also by the optical microscopy inspection, could be related to the local Cu oxidation and to oxygen intercalation after graphene growth.

KEYWORDS

chemical vapor deposition, copper foil, graphene, Raman spectroscopy, scanning tunneling microscopy

1 | INTRODUCTION

Since its first isolation by mechanical exfoliation of graphite by Novoselov et al.,^[1] graphene has been attracting enormous attention in the scientific community. In fact, thanks to its extraordinary and unique physical properties, such as outstanding thermal conductivity,^[2] high carrier mobility,^[3] and optical^[4] and mechanical features,^[5] graphene can be used for a wide range of applications as sensors,^[6,7] solar cells,^[8,9] energy storage,^[10,11] and electronic devices.^[12] Obviously, the production of graphene for commercial devices requires high quality (i.e., films free from impurities and with extended domains) and low manufacturing costs. Nowadays, among all the commonly used synthesis techniques, chemical vapor deposition (CVD) is one of the most promising to provide a proper balance between these two objectives. Indeed, CVD on transition metal surfaces is a well-suited method to large-scale production of graphene.^[13,14]

Among all the metallic surfaces, Cu is one of the most popular catalytic substrate, due to its low carbon solubility at typical growth temperatures^[15] that, at least under low pressure and ultra-high vacuum conditions, ensures a self-limited growth of graphene on its surface.^[16,17] On the contrary, graphene grown at atmospheric pressure is not self-limiting, leading to nonhomogeneous samples in which bilayer and few layer islands are present.^[18] Regardless to the growth conditions, the polycrystalline structure, the surface roughness, the presence of grain boundaries, and imperfections can affect the extension of the domains and the overall quality of the deposited layer on the copper substrate.^[19–22] In addition, the synthesis parameters, including the annealing temperature of the substrate and the sample exposure to the carbon source gas, play a leading role in the resulting quality of the graphene grown.^[23–26]

Taking into account all these aspects, in this work, graphene films on commercial copper foil were synthesized by atmospheric pressure CVD (APCVD), using CH₄ gas as carbon source diluted in a suitable mixture of Ar and H₂. The structural, morphological, and electronic properties of graphene were studied as a function of the exposure time of the metal surface to the carbon source, to determine a range of exposure times optimizing the quality of graphene films. In addition, we investigate about the two different kinds of the observed graphene, in terms of coupling with the copper surface, for the samples synthesized for exposure times between 10 and 30 min. These differences can be immediately revealed by the optical microscopy analysis and further deeply investigated by the micro-Raman spectroscopy. Finally, the statistical analysis of the Raman spectra involving the G and 2D bands Raman positions, collected on both

“coupled” and “decoupled” graphene, demonstrate the occurrence of the two different physical configurations.

2 | EXPERIMENTAL

2.1 | Film deposition

Graphene monolayer was grown on commercial Cu foil with a thickness of 25 μm and purity of 99.98% (from Matek) by catalytic CVD at atmospheric pressure condition and by using CH₄ as carbon source. The Cu surface was prepared by etching in a HNO₃ (65 wt%, Sigma-Aldrich) solution for few seconds and subsequently rinsed in distilled water. Afterwards, the substrate was rinsed again in acetone and then quickly dried, before being introduced in a carbolite furnace. The Cu foil was placed in the center of a quartz tube in an Ar–H₂ mixture at room temperature for 5 min. Then the quartz tube was loaded in a tubular horizontal CVD reactor preheated at a temperature of 766 °C, and the sample was annealed at the same temperature for 20 min under the flow of an Ar–H₂ gas mixture of 400 and 6.7 sccm, respectively. After that, the temperature was increased at the rate of 10 °C/min, from 766 °C up to 1,000 °C. At a temperature of 1,000 °C, after 10 min of annealing, the graphene growth mechanism started on Cu-foil following the addition of CH₄ (20 sccm) to the Ar–H₂ mixture. During the entire synthesis procedure, the gas were supplied at constant flow rates as indicated above. Different growth durations have been tested, ranging from 1 min to 1 hr of exposition to the CH₄ flux (for further details, see Figure 1). After any growth time, the quartz tube was extracted by the furnace and lead to room temperature (i.e., slow cooling) by flowing Ar–H₂ gases in the quartz tube.

FIGURE 1 Temperature–time diagram summarizing the different steps of the graphene growth conditions. The argon and hydrogen flows are fixed for all the steps at 400 and 6.7 sccm, respectively, whereas the CH₄ carbon source during the growth step is 20 sccm

TABLE 1 Labeling of the probed samples

Label	G1	G2	G3	G4	G5	G6	G7	G8
Growth time (min)	1	2.5	5	10	15	20	30	60

According to the growth time, samples were labeled as reported in Table 1.

2.2 | Characterization

Micro-Raman spectra were collected using a Horiba-Jobin Yvon microprobe apparatus (spectral resolution $\sim 2 \text{ cm}^{-1}$), equipped with a CCD ($256 \times 1,024$ pixels) detector cooled at -70°C , and a diode laser simulating a frequency doubled Nd-YAG laser (532 nm emission), with incident power of 50 mW. A $100\times$ Mplan Olympus objective was used (Numerical Aperture 0.90), focusing a laser spot of $2\text{--}3 \mu\text{m}$ apparent diameter. Tapping mode atomic force microscopy (AFM) and low current scanning tunneling microscopy (STM) images of the samples were acquired under ambient condition with a Veeco Multimode AFM/STM (Bruker) with Nanoscope IIIa controller and an A-type scanner. TAP150A cantilevers (Bruker) and mechanically cut Pt/Ir tips were used for the AFM and STM experiments, respectively. Scanning electron images were recorded using a Quanta FEG 400 (FEI) scanning electron microscope (SEM). The SEM images were acquired by using an electron beam ranging from 5 to 15 keV.

3 | RESULTS AND DISCUSSION

In order to get a deep understanding of our system, we used different analytic techniques to investigate the structural, morphological, and electronic features, which are related to the variable synthesis parameters of the graphene growth.

Representative SEM and AFM images of the graphene grown on Cu foil are shown in Figure 2. The heterogeneous SEM contrast at large scale, as shown in Figure 2a, is related to the polycrystalline nature of Cu foil due to electron channeling,^[27] whereas at small scale, the details about the Cu terraces are pointed out (see Figure 2b). The microstructure of the copper surface is clearly visible in the AFM analysis, where Cu terraces, almost without impurities, are evidenced (see Figure 2c). The graphene islands are not readily evident in the AFM topography images, because the surface roughness far exceeds the thickness of a graphene sheet.^[28]

The typical X-ray diffraction (XRD) patterns of the graphene samples, reported in Figure S1, show the Cu(111) crystal face for all samples at $2\theta = 43.34^\circ$. Sometimes, also the Cu(200) crystalline component is even noticeable at $2\theta = 50.44^\circ$; this is probably due to the variable heating procedure related to the graphene growth phase and confirm the polycrystalline feature of the copper foil after the annealing procedure. Furthermore, XRD extended spectra do not show any significant evidence of signals related to graphite,^[29] graphene-oxide,^[30] and Cu oxide^[31] structures.

Raman analysis was performed on all samples to point out the difference between the graphene grown at various deposition times. The shapes, the intensities, and positions of the typical Raman peaks of graphene, the D, G, and 2D bands, give a considerable amount of information on the graphene domains, including the numbers of layers and the overall quality of the film.^[32,33]

The G band is due to regular first order Raman scattering from doubly degenerate phonon mode (E_{2g}) at the Brillouin zone center, whereas the defect-activated D band corresponds to the breathing modes of six atoms rings and is generated from TO phonons around the Brillouin zone corner K.^[32–36] The 2D band, theoretically allowed independently from the crystal disorder, is an overtone of the D band. The D peak intensity is associated to the amount of defects,^[37] whereas the intensity ratio

FIGURE 2 Typical (a) large-scale and (b) small-scale scanning electron microscope images of graphene grown on Cu foil. (c) Atomic force microscopy image of graphene on Cu surface

between the 2D and G peaks changes as a function of the number of layers of the graphene film.^[38] In particular, $I_{2D}/I_G > 2$ is typical of monolayer graphene, whereas $1 < I_{2D}/I_G < 2$ indicates a bilayer deposition; if $I_{2D}/I_G < 1$, graphene film is made up of three or more graphene layers. Furthermore, the full width at half-maximum and the fitting curve of the 2D peak have to be considered to be linked at the film thickness. In fact, in the monolayer case, the 2D band is quite narrow and unimodal, and it can be fitted with a single Lorentzian component, whereas in the bilayer graphene, a wider 2D band is found that have to be fitted by four components.^[33,37] The absence of the D band in a Raman spectrum suggests a high quality graphene surface without defects, approaching the mono-crystallinity of the domains, as grain boundaries between misoriented domains within a polycrystalline domain produce a detectable D peak.^[39]

In our study, the Raman features due to the stretching mode of atmospheric molecular oxygen (O_2) and nitrogen (N_2), located at 1,555 and 2,330 cm^{-1} , respectively, are detected in all spectra. As a consequence, these bands provide surely a good internal standard frequency for the collected spectra, allowing a precise measurement of the position of the other bands. In addition, they constitute a reasonable standard for the intensity of the graphene peaks, too, because in the same focusing conditions their intensity appears to be quite

similar in all the spectra, independently on the probed graphene samples.

Raman spectra acquired on the G1 (1 min) and G2 (2.5 min) samples show similar features, and a representative spectrum is reported in Figure 3a. Here, the main Raman features of graphene are detected, though they appear broad and relatively not intense; in particular, the D, G, and 2D bands, are detectable at about 1,355, 1,590, and 2,715 cm^{-1} , respectively. These evidences suggest that the overall quality of the graphene film at 1 and 2.5 min deposition times is quite low. In this case, the signal is compatible with the presence of small graphene domains on the polycrystalline copper surface. In fact, the weak signal-to-noise ratio suggests that the surface is not completely covered by a uniform graphene film, whereas the presence of the D band points out that the small graphene domains are disordered and/or form a connected structure with an extended edge. The weak Raman signal can also be related to the coupling between graphene and Cu surface. In fact, a strong substrate-graphene coupling leads to the anti-resonance effect, which results in a weak Raman signal. A borderline case is represented by graphene growth on Nickel where no Raman signal is detected.^[40]

The evident blue shift of both G ($\sim 10\text{ cm}^{-1}$) and 2D ($\sim 15\text{ cm}^{-1}$) bands can be related in principle to several factors, including hole doping^[37,41,42] and compressive

FIGURE 3 Representative Raman spectra of graphene films grown as a function of deposition times: (a) 2.5, (b) 5, (c) 30, and (d) 60 min. Spectra were collected in the same experimental conditions

strain.^[43] A specific investigation on the peak positions issue, based on the statistical analysis of Raman spectra from many points, is developed in the following.

The Raman spectrum shown in Figure 3b is representative of a wide set of measurements, showing a variability on the 2D band in the range 2,735–2,747 cm^{-1} , whereas the G band is found between 1,610 and 1,616 cm^{-1} . For increasing growth time, the overall quality of graphene improves. Figure 3b shows the characteristic Raman spectrum of the sample synthesized at 5 min (i.e., G3 sample). The D band is still detected, but the 2D band increases its height and becomes narrower. The relatively low signal-to-noise ratio could be still related to a high graphene/Cu interaction. In this case, our interpretation of the results is that graphene domains became larger albeit some disorder is still present as pointed out by the presence of D band. Also in these cases, a blue shift of the G and 2D bands is present. Among the two cited mechanisms as cause of this shift, the compressive strain is compatible with a strong graphene/Cu interaction.

A better quality of graphene films is gained for the samples synthesized at increasing deposition time, in particular for those ranging from 10 to 30 min (G4–G7 samples). Figure 3c shows a representative spectrum collected for G7 sample (i.e., 30 min of exposure). The absence of the D band points out the lack of disorder of the graphene domains, which can be also assumed as monocrystalline,^[40] at least on the typical micrometric scale of the laser spot used in the Raman analysis. Furthermore, the narrow lineshapes as well as the intensity ratio between the 2D and G bands indicate a graphene monolayer, in which the compressive strain is still present as evidenced by the blue-shift of both bands, which could also indicate a good coupling to the substrate.

Finally, graphene quality get worse by a further increase of the growth time. In particular, the sample synthesized at 60 min shows that the graphene growth process is no more self-limiting for a long exposure to carbon precursor at ambient pressure condition, as suggested by the low ratio between the 2D and G Raman modes (<1), remarkably different from the films grown in shorter times. An additional evidence of multiple layer deposition is the increase of the overall Raman intensity of graphene bands, as revealed by the comparison with that of molecular N_2 and O_2 modes. Moreover, the resulting graphene film appears much more disordered. As shown in Figure 3d, the D band is quite strong ($I_D/I_G > 1$), indicating great number of domain edges on the deposited graphene layer, may be due to many islands growing above the underlying layers.

In summary, monolayer graphene films with optimal characteristics in terms of crystalline order are obtained

for deposition times between 10 and 30 min; for lower growth times, the graphene domains are small and disordered, whereas for longer times, the graphene growth continues beyond the monolayer, exhibiting also more structural disorder.

These optimized graphene films, synthesized between 10 and 30 min (i.e., G4–G7 samples), actually exhibit two families of Raman spectra. A typical example of the first kind of graphene spectra is the one depicted in Figure 3c, where the G and 2D bands are weak and blue-shifted. As already noted, this is linked to a strongly coupled system. The graphene areas showing this kind of spectrum are those appearing as bright extended regions as shown in Figure 4a. On the other hand, Raman spectra of the second kind are collected from the isolated darker regions in Figure 4a (some of them shown within dashed circles). A typical example of these spectra is reported in Figure 4b. It exhibits all the characteristic of an ordered monolayer graphene film. First, the intensity ratio between the 2D and G band is well above 2, whereas the D band due to the disorder or defects presence is nondetectable. Furthermore, the 2D Raman feature is unimodal, as reported in Figure S2. Finally, the peak positions of the G ($\sim 1,580 \text{ cm}^{-1}$) and 2D ($\sim 2,670 \text{ cm}^{-1}$) bands show values quite similar to those of exfoliated graphene on Si/SiO_2 .^[33,37,44] This last evidence suggests that the graphene of these dark regions is more weakly coupled to the substrate, with about the same characteristic of the free-standing one. Moreover, the signal-to-noise ratio is higher with respect to the graphene grown on the brighter regions, where the coupling to the metal substrate appears stronger. In fact, the intensity comparison between the G and 2D bands with the stretching modes of air molecules N_2 and O_2 shows it clearly (see and compare Figures 3b,c and 4b).

The G and 2D bands of “coupled” and “decoupled” regions show remarkable differences also after a quantitative statistical analysis about the peak position of the two graphene bands of the G4, G5, and G6 samples. The histograms for both G and 2D bands positions are shown in Figure 5 where it is evident that the distributions of the Raman frequencies are bimodal. This result confirms the occurrence of two physically different kind of graphene regions, characterized spectroscopically by a remarkably different peak position for both D and G band. Inside these two distinct classes, characterized by a different bond strength, associated to the coupling degree with the substrate, we have to take into account the influence of some other factor, like a spatially variable mechanical stress, responsible for the dispersion of the observed frequency values, in a way similar to that previously observed also in mechanically exfoliated graphene on Si/SiO_2 substrate.^[44]

FIGURE 4 (a) Representative optical image of the G4–G6 graphene samples (100× magnification). (b) Typical Raman spectrum from “decoupled” graphene (see dashed circle); in this case, the spectrum belongs to G5 sample

FIGURE 5 Histograms of the peak positions for (a) G band and (b) 2D band, collected both in the “decoupled” (i.e., the optical brown spots) and in “coupled” (i.e., the bright zones) graphene, for the G4–G6 samples. All curves superimposed on the histograms are normal (Gaussian) distributions. Separation between the “decoupled” and “coupled” graphene is about 12 and 28 cm⁻¹ for G and 2D bands, respectively

Another data analysis performed on the same set of samples further confirms such hypothesis. By plotting for any spectrum the 2D versus G peaks frequencies, two well distinct set of data are obtained, each one with a fairly good linear correlation (see Figure 6). In this way, we can discriminate the spectrum on the basis of the G-2D correlation, which reveals a clear discontinuity between the spectral characteristic of the optically “dark spots” (i.e., spectra of “decoupled” graphene) and those of the bright zones (i.e., “coupled” graphene to metal).

To the best of our knowledge, islands of “decoupled” regions on a “coupled” monolayer graphene have never been observed before on a copper surface at the same time. These two different graphene films can be evidenced firstly by an optical microscopy investigation and confirmed by the micro-Raman analysis.

A further in-depth investigation on the nanometer scale carried out by STM corroborates the previously reported Raman results. Indeed, a wide microscopic analysis performed over the monocrystalline graphene/Cu

FIGURE 6 Linear correlation between the G and 2D modes of graphene domains acquired on the “decoupled” (red squares) and “coupled” (black circles) regions (i.e., the optical brown and bright regions, respectively). The equations of the two linear fits are: $y_{2D} = 1.24x_G + 706.16$ (red line) and $y_{2D} = 1.47x_G + 358.50$ (black line)

FIGURE 7 (a) $4 \times 4 \text{ nm}^2$ scanning tunneling microscopy (STM) acquisition (drift corrected image) shows Moiré pattern superimposed on the atomic resolution of graphene. Tunneling parameters: $U_t = -0.03 \text{ V}$; $I_t = 0.80 \text{ nA}$. Inset: Fast Fourier transform (FFT) analysis of the STM image. (b) Graphene lattice reconstructed from the FFT analysis exhibits clearly the Moiré superstructure. (c) $4 \times 4 \text{ nm}^2$ STM drift-corrected image shows atomic resolution of graphene. Tunneling parameters: $U_t = -0.03 \text{ V}$; $I_t = 0.85 \text{ nA}$. Inset: FFT analysis of the STM image. (d) Reconstruction of graphene lattice from FFT analysis

samples (G4–G6 samples), allows identifying the two different kind of graphene. In the “coupled” graphene areas (see Figure 7a,b), a Moiré superstructure superimposed on the atomically resolved graphene is observed, due to the mismatching between the graphene and the copper surface. As a consequence, it provides a good evidence of the coupling between the two lattices. On the contrary, the absence of Moiré superstructure (see Figure 7c,d) in the “decoupled” graphene regions is compatible with a “free-standing-like” graphene.

Therefore, STM investigation confirms the presence of both “coupled” and “decoupled” graphene on the copper foil substrate. Usually, graphene grown by CVD on metal surfaces can be decoupled in presence of both oxidized surfaces and oxygen intercalation, as reported by Gottardi et al.^[45] and Voloshina et al.,^[46] respectively. In addition, the oxidation of polycrystalline copper due to the oxygen encapsulated by the graphene layer during the graphene growth could play a leading role in the graphene decoupling. In fact, as reported by a recent work of

Alvarez-Fraga et al.,^[47] the initial amount of oxygen present below the Cu surface at the grain boundaries can survive to the annealing procedure usually adopted to eliminate the surface oxide. Later, it could slowly migrate toward the surface, generating a partial re-oxidation of the copper surface below the graphene layer.

In our study, though the presence of Cu oxides grains can be excluded considering the XRD data (see Figure S1), a lasting local oxidation of copper surface and the oxygen migration after the graphene growth from the grain boundaries could play a leading role in the formation of islands of “decoupled” graphene.

4 | CONCLUSIONS

In this work, we investigated the graphene grown on copper foil by CVD at atmospheric pressure. By changing only the exposure times to the carbon precursor, we identified the optimal conditions to obtain well-ordered

monolayer graphene films, corresponding to deposition times ranging from 10 to 30 min. We find two separated areas on the monolayer graphene differentiated by the optical, Raman and STM response. The results of those techniques lead us to assign the observed contrast, in terms of graphene/Cu coupling. To the best of our knowledge, for the first time “decoupled” graphene islands on a “coupled” monolayer were found, coexisting on the Cu surface. The “decoupled” islands could be linked to the presence of Cu oxide surface areas remaining after the annealing procedure or due to oxygen migration/intercalation between the graphene layer and the metal substrate. In addition, the Raman statistical analysis performed on the “coupled” and “decoupled” graphene islands allows to unequivocally discriminate the two regions on the basis of the linear correlation between the G and 2D peak positions. Finally, a wide STM statistical analysis corroborates the previous finding.

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