Rapid and highly efficient growth of graphene on copper by chemical vapor deposition of ethanol

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Abstract

The growth of graphene by chemical vapor deposition on metal foils is a promising technique to deliver large-area films with high electron mobility. Nowadays, the chemical vapor deposition of hydrocarbons on copper is the most investigated synthesis method, although many other carbon precursors and metal substrates are used too. Among these, ethanol is a safe and inexpensive precursor that seems to offer favorable synthesis kinetics. We explored the initial stages of the growth of graphene on copper from ethanol, investigating the produced material by electron microscopy, Raman and x-ray photoemission spectroscopy. A graphene film with high crystalline quality was found to cover the entire copper catalyst substrate in just 20 s, making ethanol appear as a more efficient carbon feedstock than methane and other commonly used precursors.

1 Introduction

Graphene, the 2D material *par excellence* [1], can be grown by the catalytic decomposition of

a large variety of hydrocarbons and other carbon-containing gaseous/liquid precursors onto the surface of several metals [2]. The chemical vapor deposition (CVD) of methane (CH_4) on copper is the most common synthesis scheme, in which graphene islands start to nucleate in isolated areas and then slowly merge forming a continuous film [3-6]. The accretion process leads to the formation of a polycrystalline graphene film and has a rather slow rate, in the order of a few μm per minute [5, 6]. Consequently, the complete coverage of a copper catalyst surface takes no less than several minutes [3], although shorter process times (with rapid heating/cooling phases) are regarded as mandatory for the production of graphene for consumer devices [7]. Among the alternative precursors, ethanol (C_2H_5OH) vapor is a sensible choice [8,9] due to its safety, low cost, and easy handling. Concerning the growth rate, ethanol seems to offer different and faster process kinetics. During CVD, the ethanol vapor [10] forms a weakly oxidizing environment [11, 12] that could improve the crystalline quality, as observed for carbon nanotubes [13]. Various research groups studied the graphene growth on copper by CVD of ethanol and other alcohol precursors, exploring temperature ranges lower than those usually reported for CVD of CH_4. In particular, the 650-850°C and 900°C ranges were investigated (respectively, for 5 and 30 min growth time) [8,9]. Recently, our group reported the growth of highly-crystalline, few-layer graphene by CVD of ethanol at high temperatures (1000-1070°C), using growth times typical of CH_4-assisted growth (10-30 min) [14]. Another recent paper reported a self-limiting growth of graphene from ethanol occurring after 5 min at 1000°C; however, this was achieved in copper foil enclosures (different from plain copper surfaces), specifically designed to reduce the gas partial pressure at the catalyst surface [15].

In the present work, we report on the formation of a graphene film onto a copper surface by using ethanol, assessing if and how ethanol really promotes a faster kinetics for graphene synthesis. In our experiments, we systematically varied the temperature, the growth time and

the hydrogen dilution, investigating the coverage of the copper foil in the initial stage of the growth. We explored a synthesis time between 20 and 60 s in a high-temperature range (1000-1070°C), varying the hydrogen flow from 0 to 100 sccm.

2 Experimental

2.1 Sample Preparation Our home-built reactor consists of a high vacuum fitted, 2m long quartz tube vessel, coaxial to a 0.65 m long furnace. Other details on the experimental set-up can be found elsewhere [14]. 25 μm thick copper foil (PHC Se-Cu58, 99.95% pure) were cut to the desired size and utilized as growth substrates. In the reaction chamber the growth substrates (hosted in a quartz boat) can be quickly removed from the furnace under vacuum-tight conditions by means of a specially designed feed-through. The sample cooling is very rapid upon extraction in the cold part of the vessel, due to the intense thermal radiation and the low thermal mass of the boat.

Ethanol was contained in a steel bubbler vessel kept at 0°C (about 1500 Pa equilibrium pressure) and pressurized in Ar at 3 bar, and let into the chamber by controlling the Ar carrier flow with a mass flow controller. After reaching the desired furnace temperature (1000/1070°C), the pressure was stabilized at 400 Pa by flowing 20 sccm of Ar and 20 sccm of H_2. The ethanol-Ar flow was set to 20 sccm in all our growth experiments, thus the ethanol flow can be estimated to be 0.1 sccm. The quartz boat containing the samples was then inserted into the hot zone and annealed for 20 min at the growth temperature. Graphene was grown by switching to an the ethanol-Ar flow, and adding variable amounts of hydrogen (0, 1, 10, 100 sccm). Depending on the flows and measuring the chamber pressure the ethanol partial pressure is simply calculated between 1-2 Pa.

Such system allows performing short-duration growth experiments. The minimum process duration can be estimated by taking into account the time necessary to establish the gas flow (T1, ~15 s for a total flow of 20 sccm and a pressure of 400 Pa) and the time necessary to

move the sample to the cold zone and stop the growth (T2, less than 15 s in our system). For all this, we did not explore CVD durations shorter than 20 s.

After the synthesis, the graphene film grown on the back of each copper substrate was removed [14] and the samples were left floating onto diluted nitric acid bath (HNO_3 70%, 1:3 in H_2O) for 2 h at room temperature. After the full etching of copper, the free-floating carbon film was scooped by using a thermally oxidized silicon wafer and transferred into a clean bath of distilled water to remove etching residues. Finally, the films were transferred onto Si/SiO_2 substrates (300 nm thermal oxide) for Raman spectroscopy and Scanning Electron Microscopy (SEM), and onto nickel grids for Transmission Electron Microscopy (TEM) examination.

2.2 Sample Characterization. Raman scattering measurements were carried out at room temperature with an Instruments 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+ ion laser (Coherent Innova 70) was used to excite Raman scattering. Using a ×100 objective, the laser beam was focused to a diameter of approximately 1μm using a low laser power (below 1 mW). On each sample, the spectra were recorded at four different locations and averaged. Field Emission-SEM observations were done at low accelerating voltages (less than 1kV) with a LEO 1500 microscope with an in-line detector on as-grown and transferred samples. TEM characterization was carried out using a Tecnai F20 microscope, operated at 120 kV to reduce the radiation damage to the graphene crystals. Just before the observation, each sample was rapidly heat-treated for 10 min over a hot plate at 150 °C to reduce surface-adsorbed contaminants. X-ray photoemission spectroscopy (XPS) measurements were acquired with a VG ESCA MKII spectrometer, employing the MgKα X-ray radiation at 1253.6 eV.

3 Results

The samples were thoroughly characterized to assess the properties of the grown films (i.e., crystalline quality, domain size, thickness), and determine the overall coverage of the catalyst surface.

3.1 Optical and Secondary Electron Microscopy. In Figure 1, an optical micrograph of a film grown for 20 s (1070°C, 0 sccm H_2) and transferred onto Si/SiO$_2$ (300 nm) substrate is reported. The graphene film appears homogenous and completely covers the substrate; only a few holes and tears (lighter areas) are visible. The parallel stripes in the film are due to the lamination process of the copper foils. The film morphology carries the memory of the copper substrate texture, as evidenced by the parallel stripes (due to the lamination process during foil manufacturing) and the polygonal shapes (footprints of the copper grains). Overall, the films grown for 20 and 60 s show the same microscopic features of those grown for 10 min or more [14, 16].
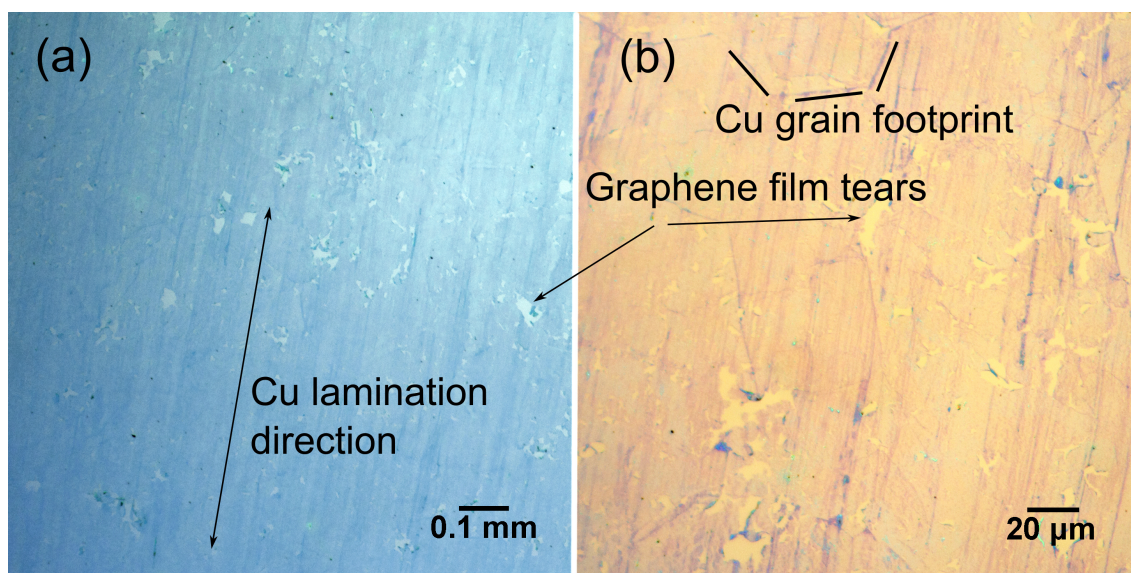

Figure 1 Optical micrograph of film grown for 20 s (1070°C, 0 sccm of H_2) transferred onto a Si/SiO$_2$ substrate at a) low and b) high magnification. Only a few tears appear in the film. Marks of the copper lamination (black double arrow) and of the copper grains (marked by while lines) are also visible.

In Figure 2, SEM micrographs of two samples grown for less than 1 min are reported. The underlying copper substrate again shows sharp grain boundaries and crystal facets. A continuous graphene film covering the copper surface is visible. The film appears polycrystalline and with a high number of wrinkles, which forms during cooling after CVD due to the difference in thermal expansion between graphene and copper [17]. The film grown in 20 s shows similar features and again covers the entire surface. Surprisingly, darker islands aligned along the lamination direction of the copper foils (white double arrows) are visible in the film, suggesting that regardless of the short time some secondary nucleation already took place. In any of our CVD experiments (even with duration of only a few seconds), it was not possible to identify individually separated graphene domains, as reported for copper enclosures with ethanol [15] or for plain copper with methane [6] and ethylene [18].
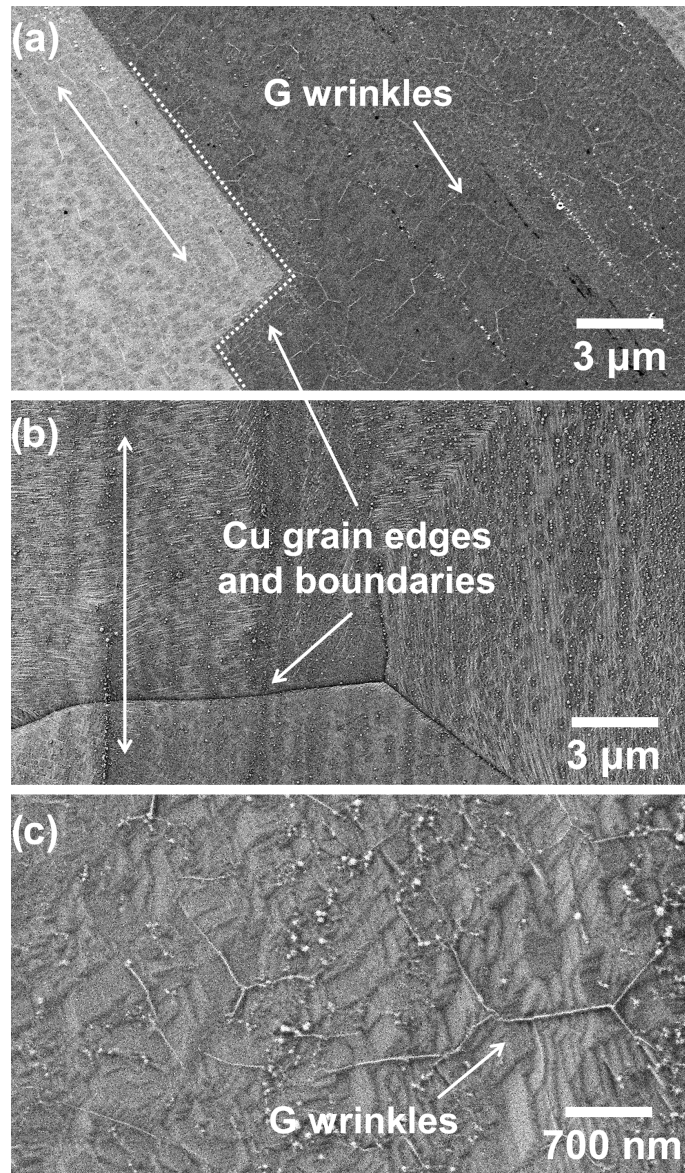
Figure 2 SEM micrographs of graphene grown on copper at 1070°C with 100 sccm H_2: a) growth for 60 s, b) and c) growth for 20 s. The white double arrows indicate the copper lamination direction. The dashed lines show the copper grain edges and boundaries. Graphene (G) wrinkles cover the entire surface.

3.2 X-ray Photoelectron Spectroscopy. A graphene film is reported to provide a barrier that retards the oxidation of copper [19]. In order to further confirm the film coverage on our copper substrates after CVD, we heated a set of samples in air at 200°C for 30 min and then verified their state of oxidation. In Figure 3 three heated samples are presented: a copper foil

with graphene grown for 10 min (Sample 1), a copper foil with graphene grown for 20 s (Sample 2), and a plain copper foil without graphene (Sample 3). The photographs of the samples show that Sample 1 and 2 retained the native metallic copper appearance regardless of the CVD time, indicating that the substrate surface was overall covered by graphene in both cases; instead, Sample 3 (only annealed in Ar/H_2 without CVD of ethanol) clearly appears oxidated.
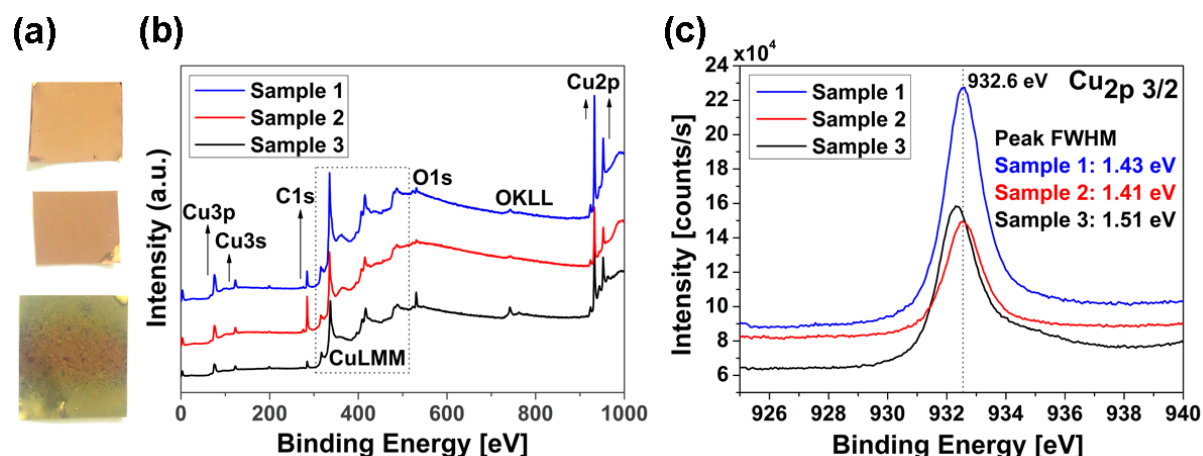

Figure 3 Copper foils after CVD and post-treatment at 200°C in air. a) Photographs of Samples 1, 2, 3 (from top to bottom). b) XPS survey scans. c) XPS carbon 1s peak. Sample key: 1) 1070°C/10 min with H_2/Ar:C_2H_5OH (10/10 sccm), 2) 1070°C/20 s with H_2/Ar:C_2H_5OH (10/10 sccm), 3) only annealing 1070°C/20 min with H_2/Ar (10/10 sccm) without ethanol flow.

The surface of the samples before and after the annealing in air at 200°C was analyzed by XPS. The survey scans of the annealed samples (Figure 3b) show the presence of copper and carbon. The oxidation state of copper could be assessed by observing both the chemical shift of the Cu $2p_{3/2}$ line (Figure 3c) and the Auger parameters of the LMM transitions (box in Figure 3b). The surface of the bare Cu sample heated at 200°C is completely oxidized, with the prevalent formation of Cu_2O. The shape of the line at higher binding energy suggests the presence of a weak CuO component too. Instead, the chemical shift and the Auger parameters

of the graphene-covered Cu samples indicate the entirely metallic nature of the surface. The lack of oxidized Cu components in the graphene/Cu sample (within the intrinsic 0.1% atomic sensitivity of the XPS) points out that the Cu foil surface is covered by graphene. We conclude that the grown film represents a sufficient barrier for such a weak oxidative process, and that the coverage of the copper catalyst during CVD occurs in 20 s as it does in 10 min. A continuous graphene film is formed over the copper surface in 20 s and less, irrespective of the hydrogen dilution both at 1000°C and 1070°C.
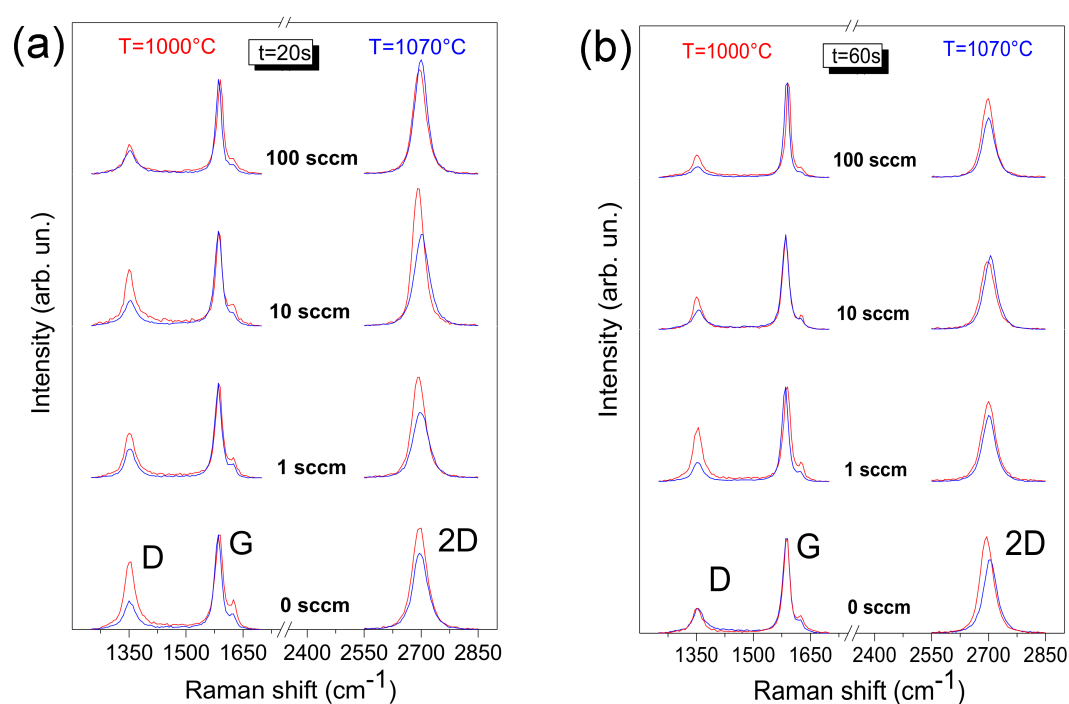
Figure 4 Raman spectra of graphene films grown for (a) 20 s and (b) 60 s at 1000°C (red curves) and 1070°C (blue curves).

3.3 Raman Spectroscopy. The graphene films, transferred onto Si/SiO$_2$ (300 nm), were further characterized by Raman spectroscopy. Figure 4 shows Raman spectra of the samples grown for 20 s (Fig.4a) and 60s (Fig.4b) at 1000°C and 1070°C for a hydrogen flow varying in the range 0-100 sccm. The main features are the G peak, centered at ~1584 cm^{-1} and the 2D peak at ~2700 cm^{-1}; D (~1350cm^{-1}) and D' (~1620 cm^{-1}) peaks are also observed, indicating

the presence of defects in the graphitic lattice, such as disordered carbon, edges and wrinkles [20, 21, 22]. Table 1 reports the I_D/I_G and I_G/I_{2D} intensity ratios corresponding to the Raman spectra of Figure 4 (the values are calculated by spectral fitting).

t (s)	Φ_{H2} (sccm)	I_D/I_G		I_G/I_{2D}	
		T=1000°C	T=1070°C	T=1000°C	T=1070°C
20	0	0.71	0.28	0.90	1.20
	1	0.47	0.32	0.91	1.35
	10	0.58	0.26	0.69	1.02
	100	0.29	0.23	0.85	0.81
60	0	0.25	0.24	0.99	1.31
	1	0.55	0.20	1.20	1.43
	10	0.34	0.20	1.32	1.27
	100	0.21	0.10	1.25	1.67

Table 1 Summary of the Raman intensity ratios for the grown films.

Lower values of I_D/I_G are obtained for longer growth times (average value of 0.27 and 0.18 at 1070°C for 20 and 60 s, respectively). It was demonstrated in previous studies that the I_D/I_G ratios reach considerably lower values when the growth time is extended up to 10 or 30 min [14, 23]. In our case, the film appears formed in either 20 or 60 s and so the graphene grains should have already grew until coalescence; therefore, the weakening of the D peak from 20 to 60 s can be explained by the reduction of defective sites in the grains, which are annealed out and cured with time. As in the case of 10 and 30 min (reported in ref. 14), the films grown at 1000°C shows I_D/I_G higher than those obtained at 1070°C (Table 1). A lower temperature is expected to promote a higher nucleation density, thus leading to smaller grains; as a consequence the density of grain boundaries increases, as reflected in a more intense D band signal. The addition of a given flow of hydrogen (Φ_{H2}) into the gas mixture is observed to reduce the I_D/I_G ratio of films grown in 60 s (especially at 1070°C), demonstrating an

improved crystalline quality. The I_D/I_G ratios of the films grown for 20 s seem instead less dependent on the hydrogen flow. The size of graphene domains (L_a) can be evaluated from the I_D/I_G integrated intensity (i.e., area) ratio according to the general equation [24]

$$L_a(nm) = 2.4 \cdot 10^{-10} \lambda_l^4 \left(\frac{I_D}{I_G} \right)^{-1}$$

where the laser line wavelength (λ_l) is expressed in nm. Figure 5 shows L_a as a function of Φ_{H2} at 1000 and 1070°C for the two growth times investigated. The graphene domain size was found to increase both with growth time and temperature.
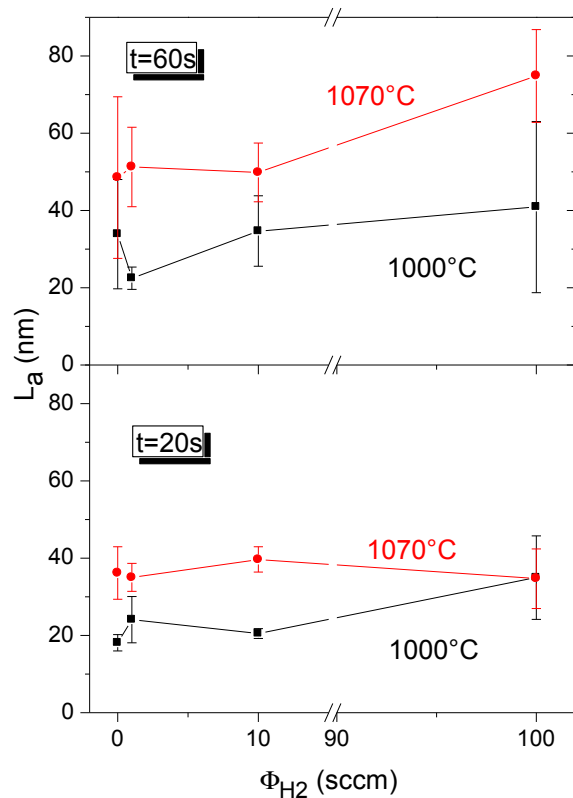

Figure 5 Graphene domain sizes of a function of Φ_{H2} for growths of 60 s (top) and 20 s (bottom).

In general, the CVD from ethanol leads to fast growth of graphene with small La, which increases with time up to around 300 nm for a growth of 10 min [14].

Qualitative information about the thickness of CVD graphene films can be deduced from the G to 2D intensity ratio (I_G/I_{2D}) [25]. The I_G/I_{2D} values reported in Table 1 are typical of few-layer graphene (1-4 layers). In particular, the ratios of the films grown for 20 s at 1000°C seem to indicate the presence of 1 to 2 layers (the I_G/I_{2D} ratio is minimum for the sample grown at 1000°C with $\Phi_{H2}=10$sccm). Overall, this shows that the growth is very fast and induces the nucleation and formation of secondary layers, as already seen by SEM (Figure 2).

3.4 **Transmission Electron Microscopy**. TEM micrographs of the same sample, shown in Figure 6, reveal that the film is well formed and continuous on the microscopic scale. Analysis of the folded edges of the graphene films allows estimating the number of layers composing the membrane (see Fig. 6-b and 6-d), confirming that the graphene films are on average composed of one to a few layers. In all cases the film is crystalline, as also shown by the diffraction pattern analysis (inset of figures 6a and 6c). We deduced that the disorder (i.e. the small domains) related to the initial growth stages of the film masks the beneficial effects of hydrogen addition observed for longer growth durations [14].
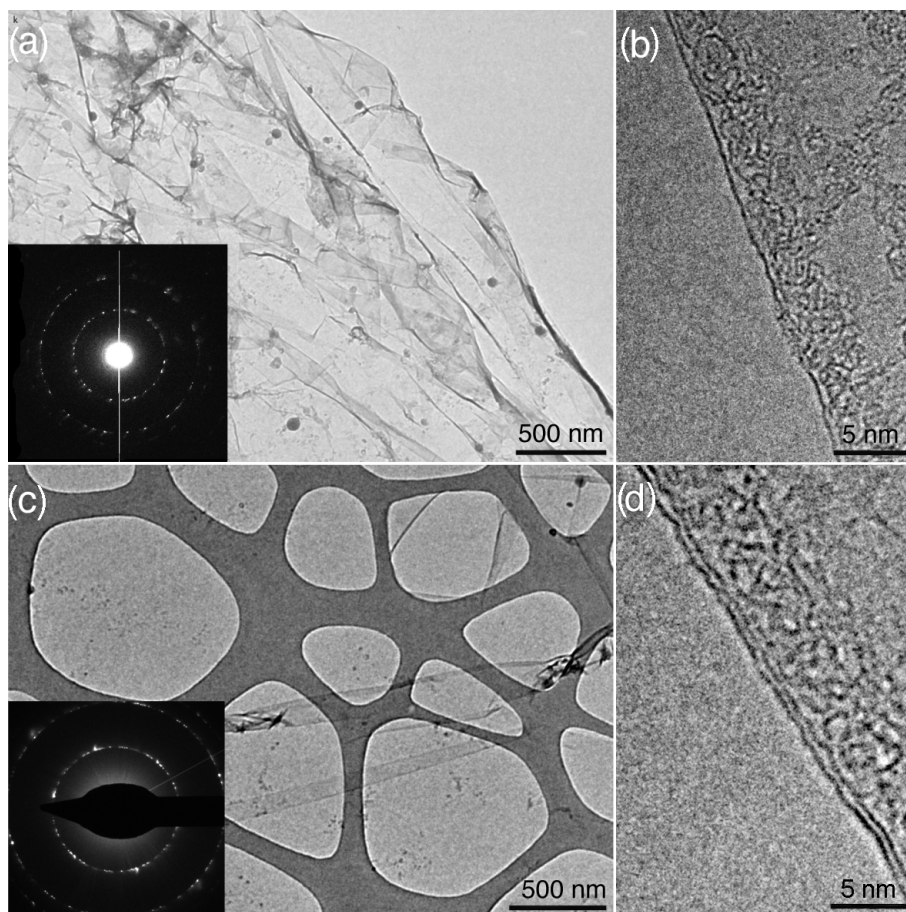
Figure 6: TEM Characterization of the graphene films transferred on TEM grids. a) Micrograph of a film grown for 20 s at 1000°C with 10 sccm of hydrogen. Inset: electron diffraction pattern of the area, showing 0.213 nm and 0.123 nm ring reflections from polycrystalline graphene film. b) High-resolution image of a monolayer graphene fold. c) Micrograph of a film grown for 1 min at 1070°C with 100 sccm of hydrogen. Inset: electron diffraction pattern of the area, showing 0.213 nm and 0.123 nm ring reflections. d) High-resolution image of a bilayer graphene fold.

4 Discussion

From the analysis of the experimental results, it appears that the CVD growth from ethanol is very rapid, and some insights in the chemistry of the growth process can be inferred. The mechanism and rate of graphene formation in CVD has been widely investigated in an extended range of conditions and for various precursors, and it has been proposed that

graphene growth might entail the direct insertion of multi-carbon radicals [26, 27]. One of the quickest CVD syntheses with methane was reported by Li et al., who grew a continuous single layer of graphene in 2 min by using a CH_4 flow of 7 sccm (6 Pa of pure methane) at 1035°C [4]. In case of CVD of ethylene, the initial stages of the growth were studied in detail up to a temperature of 950°C, with a C_2H_4 flow of 7 sccm diluted in Ar/H_2 (partial pressure of C_2H_4 of 2 Pa and total process pressure of 400 Pa) [18]: The time required to achieve the complete coverage of the copper surface was 5 minutes, comparable to that from CH_4. When using other liquid precursors, reported growth times are 4 min for n-hexane [28], 15 min for benzene [29], and 60 min for toluene [27].

As for the CVD of ethanol, some studies on the nucleation and growth kinetics of graphene appeared in the last years. Zhao et al. stated that several minutes were necessary for the formation of a complete graphene film inside "ravioli-like" copper enclosures, with an ethanol flow of 10 sccm, a partial pressure of 1 Pa and a process pressure of 300 Pa [15]. The authors also claimed incidentally that on plain copper substrates a film formed in 30 s, in line with our findings. Another group also reported the CVD growth of graphene on plain copper from ethanol in 1 min at temperatures between 850-1000°C, indicating that slightly oxidized, polycrystalline films were grown [30]. However, this fast growth was achieved at atmospheric pressure with an ethanol partial pressure of about 5000 Pa. Our experimental results further confirm and prove that the growth of graphene from ethanol is generally quicker than the growth from hydrocarbons. It is well known in literature that high temperatures induce the thermal pyrolysis of ethanol. The main products of the thermal dissociation of ethanol are ethylene (C_2H_4) and water (H_2O), while another dissociation path leads to one hydrogenated and one oxygen-containing carbon molecule [10]. In any case, during CVD the presence of an oxidizing agent can positively affect the growing carbonaceous film by removing amorphous carbon phases and preferentially etching defects, as for carbon nanotubes [13]. By contrast,

the presence of molecular oxygen, even in trace quantities, is detrimental as it leads to the etching of graphene [31]. In our perspective, the role of the oxygen should be further investigated since it might also play a role in speeding up the growth rate of graphene. It is in fact known that, when interacting with methane at high temperature, oxidized copper is covered by carbon radicals much faster than clean copper [32]; similarly, the decomposition reaction of methanol is more efficient on a partially oxidized copper catalyst in respect to clean copper [33]. Clearly, above 1000°C (1273K) in vacuum, a copper surface is entirely free from oxides, either cuprous (Cu_2O) or cupric (CuO), as predicted by the Cu/O_2 phase diagram [34, 35]. This is also the case after our CVD process, as demonstrated by our XPS analysis in Figure 3, which excluded the presence of any copper oxides on the graphene/Cu substrate. However, during CVD the amount of H_2O and CO released upon the dissociation of ethanol could instead suffice for the formation of a "temporary" Cu_2O layer on the copper substrate [34], which would be almost immediately reduced by free hydrogen atoms [36]. This oxidation/dehydrogenation process could promote the adsorption of carbon radicals on the copper surface (as happens in ref. 32) and lead to the quick formation of a graphene film. This oxide-assisted growth mechanism should be evaluated in further experiments since, if proven, it could have vast relevance for those industrial processes seeking a fast, controlled and high-yield synthesis of graphene films.

5 Conclusion

We demonstrated that fully-formed graphene films can be grown by exposing copper foils to a low partial pressure of ethanol, of 2 Pa and less, in less than 20 seconds. In such fast growth by chemical vapor deposition of ethanol, hydrogen seems to not be indispensible and have a negligible effect on the crystalline quality of graphene, in contrast to classic several-minute growths. Overall, a fast and easy synthesis method for graphene is very interesting, as it might

be potentially scalable to industrial production. The use of ethanol might also represent an advantage for high-end reactors, which can be simplified by eliminating hazardous gas lines and pressurized cylinders.

6 Acknowledgments

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