



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 growth of graphene on copper from ethanol, focusing on processes of short duration (up to one min). We investigated the produced films 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.

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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 (CH₄) 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 (C₂H₅OH) 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 of graphene, 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 CH₄ (around 1000 °C). 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 CH₄-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 quartz tube coaxial to a furnace. Other details on the experimental setup can be

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found elsewhere [14]. 25 μm thick copper foil (PHC Se-Cu58, 99.95% pure) were cut to the desired size and used 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 quartz tube, due to the intense thermal radiation and the low thermal mass of the boat.

After reaching the desired furnace temperature (1000/1070 $^{\circ}\text{C}$), the pressure was stabilized at 400 Pa by flowing 20 sccm of Ar and 20 sccm of H_2 . The quartz boat containing the samples was then inserted into the hot zone and annealed for 20 min. Ethanol (kept at 0 $^{\circ}\text{C}$ in a steel bubbler, at about 1500 Pa of equilibrium pressure) was pressurized in Ar at 3 bar and let into the chamber by controlling the Ar carrier flow with a mass flow controller. Graphene was thus grown by switching on the ethanol-Ar flow (20 sccm, with an estimated pure ethanol flow of 0.1 sccm), while adding variable amounts of H_2 (0, 1, 10, 100 sccm). Depending on the H_2 flows, the ethanol partial pressure was calculated to be between 1 and 2 Pa.

Our reactor 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 (~ 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 (less than 15 s in our system). Considering these delays, we decided to 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/SiO₂ 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 $\times 100$ objective, the laser beam was focused to a diameter of approximately 1 μm 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 1 kV) 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 $^{\circ}\text{C}$ to reduce surface-adsorbed contaminants. X-ray photoemission spectroscopy (XPS) measurements were acquired with a VG ESCA MKII spectrometer, employing the MgK α 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 Fig. 1, optical micrographs of a film grown for 20 s (1070 $^{\circ}\text{C}$, 0 sccm H_2) and transferred onto a Si/SiO₂ (300 nm) substrate are 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].

In Fig. 2, SEM micrographs of graphene on copper (samples grown for less than 1 min) are reported. The underlying copper substrate shows sharp grain boundaries and crystal facets. In all the images, 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 20-s film shows the same features of the 60-s film and likewise covers the entire substrate surface. Surprisingly, darker islands aligned along the lamination direction of the copper foils are visible in the film, suggesting that regardless of the short growth time some secondary nucleation already took place. In none of our CVD experiments (not even with duration of only a few seconds), it was 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].

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 $^{\circ}\text{C}$ for 30 min and then verified their state of oxidation. In Fig. 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 oxidized.

The surface of the samples before and after the annealing in air at 200 $^{\circ}\text{C}$ was analyzed by XPS. The survey scans of the annealed samples (Fig. 3b) show the presence of copper and carbon. The oxidation state of copper can be confirmed by observing the Auger parameters of the LMM transitions (box in Fig. 3b) and the chemical shift of the Cu 2p_{3/2} line (Fig. 3c). The surface of the bare Cu sample heated at 200 $^{\circ}\text{C}$ is

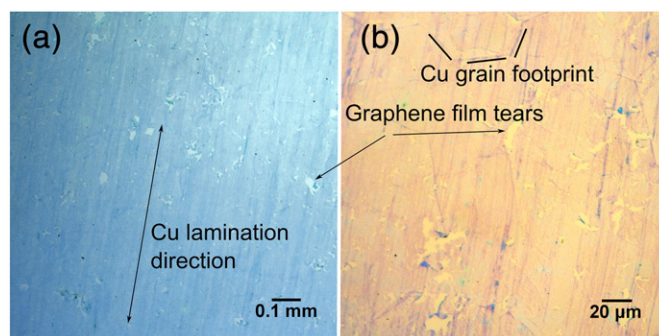


Fig. 1. Optical micrographs of a film grown for 20 s (1070 $^{\circ}\text{C}$, 0 sccm of H_2) and transferred onto a Si/SiO₂ substrate at a) low and b) high magnification. Only a few tears appear in the film. Marks of the copper lamination and of the copper grains are visible.

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