

Pressure-Controlled Chemical Vapor Deposition of Single-Layer Graphene with Millimeter-Size Domains on Thin Copper Film

Benjamin Huet*[©] and Jean-Pierre Raskin

Institute of Information and Communication Technologies, Electronics and Applied Mathematics (ICTEAM) Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

Supporting Information

ABSTRACT: In this work, single-layer graphene with compact millimeter-size domains has been obtained by chemical vapor deposition (CVD) on thin Cu film. This has been achieved by carefully adjusting the global pressure inside the CVD furnace as the graphene synthesis protocol proceeds. Global pressures in the 2-750 mbar range have been systematically investigated to determine optimal conditions for both the Cu annealing and the graphene nucleation and growth steps. It has been observed that using a high global pressure during the graphene growth is essential to grow defect-free compact domains. The low



nucleation site density, required to produce large graphene domains, has been achieved by combining a high hydrogen-tomethane ratio during the graphene growth step and an in situ Cu film oxidation induced by a high pressure level of argon during the Cu annealing step. Finally, it is found that a brief evacuation of the CVD furnace from its argon atmosphere prior to the graphene growth step is a key process step to prevent the Cu film degradation. Our method provides a scalable and reproducible way to produce high quality graphene on thin Cu film which is a convenient platform for the realization of graphene-based practical applications.

INTRODUCTION

The extraordinary physical properties of graphene, an atomically thin two-dimensional material composed of carbon atoms, make it attractive for a wide range of practical applications, particularly in the microelectronics field.¹ Up to now, chemical vapor deposition (CVD) of graphene on Cu catalyst has been considered the most promising technique to produce large-area single-layer graphene films.^{2,3} Unfortunately, CVD graphene is polycrystalline as it results from nucleation, growth, and coalescence of single-crystal graphene domains (also called grains).^{4,5} Structural defects arising from graphene grain boundaries (GGBs) are known to drastically reduce its excellent electrical and mechanical properties.⁵ The random distribution of nucleation sites and hence the random location of GGBs is particularly troublesome considering industrial fabrication of electronic devices arrays and circuits which require a high device-to-device uniformity.

The best approach to suppress GGBs-induced defects consists of significantly reducing graphene nucleation site density so that the nuclei are able to expand and eventually become large single-crystalline graphene domains (GDs). In this regard, the past 6 years have seen a substantial increase of interest in techniques leading to this goal including Cu foil pretreatments,^{6–12} customized Cu foil geometries,^{13,14} or nonconventional CVD furnace configurations.^{15–19} However, low nucleation site density cannot be reached without proper CVD processing parameters including high temperature,^{6,20,21} low methane partial pressure,^{7,20} and high hydrogen-to-

methane ratio.^{6,8,22,23} Until now, quite a few research groups achieved CVD-grown millimeter-size^{6,7,14,17,18,22,24-26} and more recently centimeter-size GDs^{9,11,27} on Cu foils. These results are summarized in Table S1 in the Supporting Information.

In contrast to widely spread Cu foils, using a thin Cu film deposited on a flat, smooth, and rigid substrate offers exciting prospects for various reasons: (i) given its fabrication process and its quasi two-dimensional nature, the Cu film features a higher purity and, more particularly, a lower carbon content which can yield an intrinsically lower nucleation site density and reduce the chance of producing a few-layer graphene; (ii) its relatively smooth surface morphology circumvents the use of cumbersome pre-CVD treatments required to eliminate the surface morphology singularities which can act as preferential sites for graphene nucleation;²⁸ (iii) heteroepitaxial Cu film can be used to control the orientation of graphene domains; 2^{29-31} (iv) using a flat and rigid substrate improves graphene processability as it allows the direct processing of graphene by conventional CMOS technologies;³² (v) as graphene growth mimics Cu surface morphology, producing graphene on a smooth and flat Cu film results in a more planar graphene sheet and, in turn, less wrinkles and cracks in the transferred graphene.³³ It is also worth mentioning that Cu films deposited

Received:November 19, 2016Revised:March 6, 2017Published:March 11, 2017



Figure 1. Millimeter-size graphene domains grown on 1.2 μ m thick Cu film. (a) Photograph of a Cu film evaporated on a 3 in. quartz wafer after a 30 min graphene growth and post-CVD Cu oxidation to make graphene visible. (b) Optical microscopy image of millimeter-size GDs as grown on Cu film after Cu oxidation. (c) SEM image of a graphene domain as-grown on Cu film with hexagon-like edges. (d) Higher magnification SEM image corresponding to the framed area in panel c. (e) Optical microscopy image of GDs transferred on a 90 nm thick SiO₂/Si substrate. (f) Higher magnification image of transferred graphene indicated in the framed area in panel e; the dashed circle highlights a small bilayer dot.

on an inert substrate have only one single surface exposed to the CVD furnace atmosphere and prone to produce C species. As a result, graphene growth is exclusively dictated by surface reaction and does not depend on C species diffusion through the catalyst thickness.³⁴ Cu films thus constitute an ideal alternative to Cu foils for rigorously studying the influence of CVD conditions on graphene growth.

To our knowledge, the largest graphene domains ever grown on thin Cu film reached a maximum lateral size of 100 μ m and a few hundreds of micrometers for domains with compact hexagonal^{29,30} and dendritic^{23,31} shapes, respectively. The key challenge for growing millimeter-size GDs on Cu film lies in maintaining the Cu film's physical integrity upon the high temperature CVD process while using appropriate CVD conditions. Cu film degradation arises mainly from Cu evaporation loss,³⁵ Cu film dewetting,³⁶ or Cu interdiffusion with the underlying substrate.³⁷ A shorter duration or a reduced temperature for the graphene growth step has been used to grow graphene while mitigating Cu degradation, but these conditions are conflicting with the growth of compact large domains.^{38,39}

Here we controlled the global pressure inside the CVD furnace to determine optimal conditions during Cu substrate annealing, graphene nucleation, and graphene growth. Thanks to properly adjusted CVD parameters, we demonstrate for the first time the growth of compact millimeter-size graphene single crystals on top of thin Cu films. We first conducted a systematic study of the impact of the hydrogen-to-methane ratio (ranging from 2 to 1100) under various global pressure conditions (from

2 to 750 mbar) on graphene nucleation site density and the domain growth front. Our results suggest that a low nucleation site density can be achieved under both low and high pressure conditions provided that methane partial pressure is close enough to the nucleation threshold. However, higher global pressure conditions are more appropriate to achieve high H₂-to-CH₄ ratios which favor the growth of high structural quality GDs with a compact shape. We also show that using a higher pressure of argon during the Cu catalyst annealing/ramping step efficiently contributes to the reduction of the nucleation site density. Finally, we found out that when using a high Ar pressure level during the CU annealing step, it is essential to temporarily evacuate the CVD chamber prior to the graphene growth step in order to avoid Cu film degradation.

RESULTS AND DISCUSSION

Demonstration of Millimeter-Size GDs. Photograph (Figure 1a), optical microscopy image (Figure 1b) and scanning electron microscopy (SEM) images (Figure 1c,d) show millimeter-size graphene domains as produced on a 1200 nm thick Cu film deposited on a 3 in. quartz wafer. Graphene is made visible directly after the CVD process by heating the substrate on a hot plate at 150 °C for 5 min in air as shown in Figure 1a,b.⁴⁰ A 30 min growth step results in graphene domains of a few hundreds of micrometers that can be easily distinguished from each other with bare eyes as shown in Figure 1a. Extended graphene growth durations result in graphene domains with lateral size exceeding 1 mm after about 1 h (see Figure 1b) and the completion of a continuous



Figure 2. Graphene growth evolution with global pressure and H_2 -to- CH_4 ratio. (a) Temperature, gas flow, and global pressure profiles used for the CVD experiments. (b) log-log plot summarizing the global pressure and the H_2 -to- CH_4 ratio conditions used for the different CVD experiments. (c-f) SEM images of graphene grown on Cu under pressures of (c) 8, (d) 20, (e) 100, and (f) 750 mbar. Panels g-j are higher magnification SEM images of the framed square areas in panels c-f, respectively.

graphene sheet after about 90 min. Graphene domains exhibit a rather compact shape consisting of a mixture of rounded and straight edges forming $\sim 120^{\circ}$ corners similarly to hexagons.

The hexagon-like shape of GDs, indicating a coherent atomic structure within the entire domain, suggests that these domains are single-crystalline. The non strictly straight growth front and hexagonal shape of graphene domains grown on Cu films most likely result from the fact that these GDs span over several adjacent Cu grains when they reach a lateral size of about 1 mm. These different Cu grains can be responsible for slight local variations in growth condition as different Cu surface crystallographic orientations present different catalytic activities, diffusion rates for adsorbed species, and carbon precursor adsorption/desorption rates.^{41–43} Except the bilayer regions with lateral size of a few micrometers occasionally found near the graphene domain edges (see dashed circle in Figure 1f), the clear uniform color contrast shown in the SEM images (Figure 1c,d) and optical microscopy images of graphene transferred on a 90 nm thick SiO₂/Si substrate reflects the single-layer nature of the produced graphene sheet. Although the Cu film's intrinsic high purity and smooth surface morphology may contribute to the suppression of nucleation sites, the successful growth of compact large-area GDs mainly results from the appropriate adjustment of the CVD conditions inside the furnace during the CVD process (see Supporting Information section S2).

Graphene Growth Pressure. The first step toward the synthesis of such large-area compact single-layer GDs consists

of determining the CVD processing parameters (temperature, global pressure, and gas flows) and more particularly the graphene growth conditions (CH₄ partial pressure, H₂-to-CH₄ ratio, temperature, and global pressure) favoring a low density of nucleation sites as well as a nondendritic growth front. In contrast to previously published works which studied the graphene growth under strictly low pressure (LP) condi-tions^{13-15,17,20,25} or ambient pressure (AP) conditions,^{7,11,24,44} we investigated the growth of graphene under different pressure levels ranging from 2 to about 750 mbar. In order to determine which pressure range is the most appropriate to produce large GDs, we compared the nucleation site density that can be achieved at different global pressures under optimal methane partial pressure, that is, under a partial pressure as close as possible from the nucleation threshold. Using a methane partial pressure (P_{CH_4}) far beyond the threshold would result in excessive adsorption of methane molecules on the Cu surface, in a higher supersaturation of C species and, in turn, in the formation of a high density of nucleation sites.²¹

Predicting the methane partial pressure corresponding to the nucleation threshold is challenging since it strongly depends on many factors including the catalytic substrate preparation and the desorption rate of active C species from the Cu surface (which is mainly dictated by the CVD furnace temperature and global pressure). Therefore, several experiments with a precise control of the methane partial pressure have been carefully conducted to determine an approximate value of the lowest $P_{\rm CH_4}$ allowing the nucleation of graphene. The precise

monitoring of $P_{\rm CH_4}$ is achieved by tuning the injection of Ar/H₂ ($F^{\rm Ar/H_2}$) and Ar/CH₄ ($F^{\rm Ar/CH_4}$) gas flows into the CVD furnace and is calculated according to

$$P_{\rm CH_4} = P_{\rm tot} \frac{F^{\rm Ar/CH_4} D^{\rm CH_4}}{F^{\rm Ar/CH_4} + F^{\rm Ar/H_2}}$$
(1)

where D^{CH_4} is the dilution of the Ar/CH₄ (2500 ppm) gas flow feedstock used in this work. For a given global pressure (P_{tot}), using a higher Ar/H₂ gas flow results in a higher dilution of the methane in the gas phase (i.e., a lower methane partial pressure) and a higher hydrogen-to-methane ratio (R) which is calculated by

$$R = \frac{F^{\rm Ar/H_2} D^{\rm H_2}}{F^{\rm Ar/CH_4} D^{\rm CH_4}}$$
(2)

where D^{H_2} is the dilution of the Ar/H₂ (10%) gas mixture feedstock.

The temperature, gas flows, and pressure profiles used for this investigation are illustrated in Figure 2a. To provide a rigorous analysis, the Cu film annealing step is performed under the exact same conditions, regardless of the pressure used for graphene growth. Once the graphene growth temperature ($T_{\rm gr}$ = 1050 °C) is reached, Ar/H₂ and Ar/CH₄ gas flows are introduced in the CVD furnace and the aperture of the metering valve located downstream of the CVD furnace is adjusted. The pressure increases and stabilizes at a value determined by the metering valve aperture and the total gas flow introduced. Using low pressure conditions prior to the introduction of methane and hydrogen ensures that the gas phase composition inside the CVD furnace during the growth stage is exclusively dictated by the gas injected since the beginning of the growth stage.

Figure 2b summarizes the outcome of the graphene growth experiments conducted in this work. Although no graphene formation has been observed for graphene growth performed at 2 mbar, graphene has been synthesized under various H₂-to-CH₄ ratios for all the pressure levels investigated here including 8, 20, 100, and 750 mbar. Low methane dilution levels result in continuous graphene sheets (green circles) while excessive methane dilution levels do not yield any graphene formation (red crosses). Intermediate dilution levels (blue squares) correspond to the growth of graphene nuclei which are sufficiently separated from each other that individual GDs can be observed by means of the SEM. Nucleation site density and the domain size plots corresponding to these experiments are displayed in Supporting Information section S3. Since a low nucleation site density (≤ 0.05 nuclei/mm²) can be obtained for all pressure levels investigated here including 8, 20, 100, and 750 mbar, it seems that the global pressure is not a decisive parameter for the lateral size of produced GDs.

More interestingly, Figure 2b shows that graphene formation can be achieved under higher H_2 -to- CH_4 ratios when the CVD process is performed under higher global pressure. The maximum H_2 -to- CH_4 ratio that can be used to produce graphene shifts from about 200 to 700 when the global pressure is raised from 8 to 20 mbar and can even reach about 1100 when the global pressure equals 100 mbar (more details in Supporting Information section S3). Increasing the pressure and the H_2 -to- CH_4 ratio clearly affects the growth of graphene as shown in Figure 2c–f that have been produced at 8, 20, 100, and 750 mbar, respectively. Even though graphene domains grow in a form tending to hexagon-like shapes (Figure 2c–f) indicating a coherent atomic structure, the growth front differs a lot (Figure 2g-j). Producing graphene at a relatively low pressure results in a highly dendritic growth front and partially hollow graphene domains (as shown in Figure 2c,d). Increasing the global pressure and the H₂-to-CH₄ ratio yields denser graphene domains (i.e., featuring thinner graphene-free veins) as well as smooth edges. Although the dendritic aspect can be reduced by increasing the H2-to-CH4 ratio while maintaining the same global pressure, this ratio has to remain relatively low to avoid excessive dilution of methane and allow graphene formation. Furthermore, our experiments show that even if the H_2 -to-CH₄ ratio is exactly the same (R = 800 in Figure 2e,f), an increase of global pressure produces smooth edges instead of jagged edges. As a consequence, we believe that using higher pressure conditions is a key CVD parameter for the growth of high quality graphene.

The significant modification of graphene crystal morphology with the global pressure and H2-to-CH4 ratio can be explained by considering the interplay of complex processes including the diffusion of active C species adsorbed on the Cu surface, the attachment of these C species on the growing GD and the competition between the growth and etching of graphene induced by the presence of hydrogen in the gas phase.²³ ' The highly dendritic front obtained at lower pressure most likely arises from the combination of a relatively low concentration of active C species adsorbed on the Cu surface and a relatively high growth rate of the branches of GDs. The low pressure conditions favor a low concentration of C species due to a low adsorption rate of methane (resulting from a low partial pressure in the gas phase) and a high desorption rate of C species (induced by Cu sublimation). On the other hand, the etching effect of hydrogen has a limited impact due to the low amount of hydrogen present in the gas phase. As a result, graphene protrusions in the growth front propagate radially and deplete their surrounding in C species. This depletion hinders the lateral growth of dendritic graphene branches and the formation of dense GDs. On the contrary, the smooth edges and dense graphene domains achieved under relatively high pressure conditions and high H2-to-CH4 ratios are most likely the result of a relatively high concentration of C species on the Cu surface available for the formation of graphene and a strong competition between graphene growth and graphene etching at the growth front.

Annealing Pressure. Another major milestone toward the synthesis of large-area GDs consists of decreasing the nucleation site density by employing appropriate conditions during the warming ramp of the CVD furnace. Although the pioneers of CVD growth of graphene on Cu used it to introduce hydrogen during the warming ramp, 2,20,32,46 recent works suggested that using a pure Ar flow is more convenient to obtain large graphene single crystals^{11,22,24} (see Supporting Information section S4). We demonstrate here that the Ar pressure levels present in the CVD furnace during the warming ramp of the CVD protocol significantly affect graphene nucleation density. To illustrate this statement, we performed a series of graphene growth experiments with an identical graphene growth step but different annealing pressure conditions. In order to apply the exact same graphene growth conditions (temperature, global pressure, and gas composition profiles) in each experiment regardless of the Ar pressure used during the annealing, the CVD furnace is evacuated for 5 min prior to the introduction of hydrogen and methane as shown in Figure 3a. Figure 3b represents the evolution of nucleation site



Figure 3. Impact of Ar pressure during the Cu annealing/ramping step. (a) Temperature, gas flow, and global pressure profiles used for the various CVD experiments. (b) log–log graph showing the nucleation site density evolution with the Ar pressure level used during the Cu annealing/ramping step. (c–f) Optical microscopy images of samples annealed under 20 (c), 50 (d), 200 (e), and 500 mbar (f) of argon, respectively.

density with the Ar pressure used during the Cu annealing step. The nucleation site density values have been estimated by manually counting the graphene domains made visible by a slight oxidation of the Cu surface. The counting has been carried out by observing four areas of ~ 1.2 cm² randomly chosen on the 3 in. catalytic wafer ($\sim 44 \text{ cm}^2$) used for the experiment. Due to rather small variation in local graphene nucleation site density, the four estimated dots might overlap and not be visible for each annealing global pressure level. Our observations clearly show a drastic drop of the nucleation site number by nearly 3 orders of magnitude when Ar pressure is increased from 2 up to 750 mbar. Optical microscopy images corresponding to Ar annealings of 20, 50, 200, and 500 mbar are showed in Figure 3c-f, respectively. It can also be observed by comparing Figure 3c to Figures 3d-f that using a higher Ar pressure upon the Cu annealing decreases the apparent graphene growth rate. This tendency is particularly noticeable for relatively low Ar pressure, that is, in the 2-50 mbar range.

The actual effect of argon pressure on graphene growth has been further investigated by observing the evolution of the Cu surface prior to any graphene formation. We mainly focus on the two extreme cases presented in Figure 3a, namely, the CVD protocols involving an annealing step under relatively low pressure (2 mbar) and under relatively high pressure (750 mbar) of argon. First, we observed the Cu surface directly after the annealing step by carrying out the experiments illustrated in Figure 4a. As shown in Figure 4c,d, heating the Cu substrates in an Ar atmosphere creates a colorful compound on the Cu surface. Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) have been used to identify the nature of this compound which turns out to be copper oxide (see Supporting Information section S5). The amount of copper oxide produced during the annealing step seems to depend on the argon pressure as low pressure conditions (2 mbar) yield only a few copper oxide islands while high pressure conditions (750 mbar) result in the formation of an almost continuous copper oxide layer. Although the argon supply used here is supposed to be inert and pure (Ar 6.0 Research grade, 99,9999% pure, Praxair), it appears to have a slight oxidizing effect. This effect, probably due to the presence of oxidizing impurities (H₂O < 1 ppm, O₂ < 0.2 ppm), increases with global pressure.

Recently, a few research groups demonstrated that mildly oxidizing the Cu catalytic surface effectively contributes to decreasing the nucleation site density.^{9,11,12,22,24,25,47} However, these works differ on explaining how oxygen actually impacts the synthesis substrate and graphene growth. The reduction of nucleation site density has been ascribed to (i) a modification of Cu surface morphology,^{24,25} (ii) the presence of a catalytic inactive oxide layer at the beginning of graphene growth,²² (iii) the passivation of Cu active sites,^{9,11} (iv) the removal of surface impurities,^{25,47} and (v) the reduction of the carbon content in the Cu catalyst.^{12,47} To better understand how the use of an



Figure 4. Impact of ramping/annealing the Cu substrate under an Ar atmosphere on the suppression of nucleation sites. (a) Temperature and pressure profiles of a first set of experiments used to determine how Ar atmosphere affects the Cu surface during the warming ramp. (b) Temperature and pressure profiles of a second set of experiments used to get an insight on how the Cu surface evolves at the onset of the graphene growth step. (c, d) Optical images of the Cu surface after the experiment described in panel a under Ar pressures of (c) 2 and (d) 750 mbar. (e, f) Optical images of the Cu surface after the experiment burger of the pressure of the first of the cu surface after the experiment described in panel burger of (e) 2 and (f) 750 mbar.

oxidizing atmosphere during the annealing step plays a role in drastically reducing the nucleation sites during the graphene growth step, we focus on how the catalytic substrate evolves in the very early stage of the graphene growth step, that is, when Ar/H_2 and Ar/CH_4 flows are injected inside the CVD furnace.

In this regard, we performed the exact same experiments as in Figure 3 but interrupted the graphene growth step after a 10 min exposure to the reducing atmosphere composed of H_{2i} CH_4 , and Ar (see Figure 4b). This short duration growth step does not trigger any graphene growth, most likely because the Cu surface is not exposed for a sufficient time to the carbon source to start the nucleation. To ensure no extra oxidation/ reduction during the cooling step in the CVD protocols displayed in Figure 4a,b, the furnace is rapidly evacuated down to a pressure of 1 mbar. As a consequence, observing the Cu substrate after these experimental tests provides an insight into the Cu surface condition shortly before the onset of graphene formation. It appears that the copper oxide induced during the annealing step completely vanished, probably turned into metallic Cu due to the reducing atmosphere. Additional experiments also showed that the continuous oxide layer obtained by annealing the Cu under 750 mbar of argon was getting completely reduced upon the first 2 min of exposure to the reducing atmosphere (results not shown). These observations suggest that the copper oxide layer does not directly interact with the growth of graphene and cannot act as a reversible passivation layer which gradually vanishes as

graphene growth proceeds as any traces of copper oxide are reduced way before graphene formation starts.

Although the Cu surface morphology and oxidation level differ a lot depending on whether it has been annealed under 2 or under 750 mbar of argon, it is relatively similar once the Cu substrates have been exposed to the $Ar/H_2/CH_4$ gas mixture for 10 min (Figure 4e-,f). The formation of more copper oxide during the warming ramp hinders the Cu grain microstructure evolution upon annealing and lead to puddles of smaller Cu grains (Figure 4f). However, no correlation has been found between these puddles and the location of graphene nuclei. Moreover, no Cu surface singularities/protrusions have been observed in the center of the graphene domains as observed on Cu foils by Luo's group.²⁴ Therefore, we do not believe that a surface morphology modification is the key factor for reducing the nucleation site density by almost 3 orders of magnitude.

We believe that the nucleation site density is strongly affected by the accumulation of active C-based species on the Cu surface during the annealing step. These C-based species may originate from various sources including (i) the pyrolysis of organic compounds introduced in the CVD furnace during the loading of the synthesis substrate, (ii) previous graphene growth processes which brought C-based compounds inside the furnace (through methane cracking, particularly promoted by evaporation/re-deposition of Cu on the inner walls⁴⁸), or even (iii) directly from the bulk of the Cu catalyst as proposed by Kraus et al.,¹² which is the less likely reason here given the



Figure 5. Raman measurements of single crystals of graphene. (a) Optical microscopy image of graphene transferred onto a 90 nm thick SiO₂/Si wafer. (b) Raman spectra acquired in the different locations denoted by color dots in panel a. (c-f) 50 × 60 μ m² Raman mappings corresponding to the areas highlighted by the insets in panel a. I_{2D}/I_G and I_D/I_G mappings taken (c, d) along the GD edge and (e, f) at the center of the domain.

thickness and the fabrication process of the Cu film (see Supporting Information section S6). During the annealing, organic compounds vaporize in the gas phase and preferentially react on the catalyst. When annealed in an Ar atmosphere, the Cu surface gradually oxidizes (through the presence of oxidizing agents present in the Ar feedstock) and forms a reversible passivation layer which reduces the accumulation of C-based species on the surface. Moreover, the oxidizing agents contribute to neutralizing organic compounds (through formation of CO and CO_2) present in the furnace.⁴⁷ We believe that both the oxidative removal of C atoms in the CVD furnace and the C-species impoverishment on the Cu surface induced by the copper oxide passivation layer effectively contribute to lowering the nucleation site density. This effect is even more significant as the Ar pressure (i.e., the oxidizing effect) is important. The high nucleation site density obtained following a Cu annealing in a reducing atmosphere can be explained by the formation of highly volatile hydrocarbons (C_rH_v) produced by H₂-induced etching of existing graphene in the furnace or newly created by reduction of freshly introduced parasitic organic compounds (see Supporting Information section S4). Moreover, maintaining a reduced Cu catalytic surface makes it more reactive for catalyzing the undesired Cbased compounds transported by the gas phase.

The manifestation of a more effective C species depletion on the Cu surface with higher Ar pressure during the annealing can also be observed in Figure 3c-f. Given that the growth conditions are exactly the same in the different CVD experiments, it is unlikely that the different domain sizes arise from different graphene growth rates. The smaller domain size achieved on the Cu substrate annealed under an Ar pressure equal or greater than 50 mbar is most likely induced by a graphene nucleation delay compared with the Cu substrate annealed under lower Ar pressure. Intuitively, a Cu substrate which is depleted in C species at the onset of the graphene growth step will require a longer duration to catalyze methane and achieve a sufficient concentration of C-based species to trigger graphene nucleation.

From the above observations, it might be tempting to perform both the Cu annealing and the graphene growth at high pressure, without proceeding to the evacuation of the chamber prior to the graphene growth step (shown in Figures 2, 3, and 4). However, it has been observed that directly introducing methane and hydrogen in the CVD furnace containing a high pressure of Ar results in the Cu film solidstate dewetting (see Supporting Information section S7). Dewetting of thin Cu films upon the CVD process has already been observed and attributed to excessive Cu evaporation induced by high temperature and low pressure conditions used for graphene growth.³⁶ Here, we intentionally use Cu films with a thickness of at least 1 μ m and limit the high temperature step duration to a maximum 90 min to deal with the sublimationinduced Cu film dewetting issues. Moreover, it is unlikely that the excessive Cu sublimation is responsible for the dewetting observed here as it occurs at the onset of the graphene growth step. It is found that the dewetting stage depends on the Ar pressure used during the Cu annealing step and no dewetting is observed for Ar pressure levels under 10 mbar. It is believed that the Cu dewetting results from the reaction between hydrogen absorbed from the atmosphere and oxygen present inside the copper film which forms water vapor that decreases the cohesion between Cu grains. This phenomenon, called hydrogen embrittlement, is known to make bulk metals porous upon hydrogen annealing.⁴⁹ It seems that the presence of the copper oxide thin layer on the Cu top surface does not play a role as evacuating the chamber does not remove that oxide layer. However, evacuating the furnace for 5 min might either reduce the oxygen content in the Cu film or slow down the arrival of hydrogen on the Cu surface and thus prevent any formation of water vapor in the Cu matrix. As a consequence, the evacuation of the CVD chamber prior to graphene growth is always performed to obtain millimeter-size GDs.

Graphene Transfer and Raman Analysis. Further characterization is achieved by transferring as-produced graphene from the Cu film onto 90 nm thick SiO₂/Si wafers. In order to evaluate the structural quality and number of layers, Raman spectroscopy measurements have been performed on the two transferred GDs presented in Figure 5a. Figure 5b displays stacked Raman spectra corresponding to the different locations identified by colored dots in Figure 5a. These spectra were acquired using a 2400 grooves/mm grating in order to obtain precise values of the peak positions and full width at half-maximum (fwhm). Each spectrum exhibits a 2D peak (with a position varying from 2670 to 2690 cm^{-1}), a G peak (1577– 1582 cm⁻¹), and a very weak D peak (1337–1341 cm⁻¹) which suggests an insignificant amount of structural defects. The intensity ratio I_{2D}/I_G about 2, the relatively narrow 2D peak (fwhm_{2D} ranging from 34 to 42), and the fact that the 2D peak can be fitted by one single Lorentzian component indicate that the GDs are monolayer.^{50,51} The observed shift of the peaks is more likely due to mechanical stress and/or doping induced by the transfer process steps (see Supporting Information section S8).⁵²

To further assess the spatial uniformity of graphene quality and thickness within a single GD, Raman mappings have been acquired on 50 \times 60 μ m² areas located in the center and at the periphery of the GD as shown by the insets in Figure 5a. Regardless of whether the mapping is acquired at the periphery (Figure 5c,d) or at the center (Figure 5e,f), the intensity of the D peak is almost 2 orders of magnitude smaller than that of the G peak (except in the transfer process-induced cracks that are visible in the insets of Figure 5a). Both mappings also exhibit a 2D to G intensity ratio ranging from 1.7 to 2.5, which suggests the absence of bilayers regions in these locations. Raman coherent information and, hence, uniform graphene quality and thickness over the GD surface demonstrate a good consistency in the growth conditions as the GD formation proceeds. This confirms our aforementioned observations stating that even if the GDs shapes are not completely hexagonal, individual millimeter-size graphene domains originate from a single graphene nucleus.

CONCLUSION

In conclusion, we developed a new CVD approach to produce single-layer graphene sheets with millimeter-size graphene domains on thin Cu films. This innovative approach is based on the continuous regulation of global pressure inside the furnace during the CVD synthesis protocol. Adjusting the global pressure allowed us to find optimal conditions for both the Cu annealing/ramping and the graphene nucleation/ growth steps. Our findings suggest that the global pressure during graphene growth does not play a major role in determining the nucleation site density and hence the maximum dimensions of graphene domains. However, using high pressure levels is a key graphene growth condition to yield defect-free graphene domains with compact shape and smooth edges. On the other hand, we observed that annealing the Cu substrate in an Ar atmosphere is essential to obtain large-area graphene domains and higher Ar pressure conditions favor a

low density of nucleation sites. Finally, we found out that evacuating the CVD furnace for 5 min prior to graphene growth is an effective way to address the dewetting issues observed when a high pressure of Ar is used during the Cu annealing step. Thanks to these considerations, we are able to routinely produce millimeter-size single crystals of graphene on a thin Cu film which is a more suitable platform than Cu foils for the implementation of graphene-based practical applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b04928.

Additional graphene growth results on Cu films and Cu foils and detailed material and methods (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: benjamin.huet@uclouvain.be. Phone: +32 (0)495 444 269.

ORCID [©]

Benjamin Huet: 0000-0003-4084-5705

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the financial support from the Fonds Nationaux de la Recherche Scientifique (FNRS-Belgium), the Fonds pour la Formation à la Recherche dans l'Industrie et dans l'Agriculture (FRIA-Belgium), and the Actions de Recherche Concertées ARC "StressTronics" and "NATURIST" projects granted by the Communauté française de Belgique. In addition, we gratefully acknowledge the Wallonia Infrastructure for Nano FABrication (WINFAB) for the equipment and the Wallonia ELectronics and COMmunications measurements (WELCOME) platform for the micro Raman system.

REFERENCES

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(2) Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312–1314.

(3) Ren, W.; Cheng, H.-M. The Global Growth of Graphene. *Nat. Nanotechnol.* **2014**, *9*, 726–730.

(4) Huang, P. Y.; Ruiz-Vargas, C. S.; van der Zande, A. M.; Whitney, W. S.; Levendorf, M. P.; Kevek, J. W.; Garg, S.; Alden, J. S.; Hustedt, C. J.; Zhu, Y.; Park, J.; McEuen, P. L.; Muller, D. A. Grains and Grain Boundaries in Single-Layer Graphene Atomic Patchwork Quilts. *Nature* 2011, *469*, 389–392.

(5) Yazyev, O.; Louie, S. G. Electronic Transport in Polycrystalline Graphene. *Nat. Mater.* **2010**, *9*, 806–809.

(6) Yan, Z.; Lin, J.; Peng, Z.; Sun, Z.; Zhu, Y.; Li, L.; Xiang, C.; Samuel, E. L.; Kittrell, C.; Tour, J. M. Toward the Synthesis of Wafer-Scale Single-Crystal Graphene on Copper Foils. *ACS Nano* **2012**, *6*, 9110–9117.

(7) Zhang, Y.; Chen, Z.; Wang, B.; Wu, Y.; Jin, Z.; Liu, X.; Yu, G. Controllable Growth of Millimeter-Size Graphene Domains on Cu Foil. *Mater. Lett.* **2013**, *96*, 149–151.

(8) Mohsin, A.; Liu, L.; Liu, P.; Deng, W.; Ivanov, I. N.; Li, G.; Dyck, O. E.; Duscher, G.; Dunlap, J. R.; Xiao, K.; Gu, G. Synthesis of Millimeter-Size Hexagon-Shaped Graphene Single Crystals on Resolidified Copper. *ACS Nano* **2013**, *7*, 8924–8931.

(9) Hao, Y.; et al. The Role of Surface Oxygen in the Growth of Large Single-Crystal Graphene on Copper. *Science* **2013**, 342, 720–723.

(10) Wang, H.; Wang, G.; Bao, P.; Yang, S.; Zhu, W.; Xie, X.; Zhang, W.-J. Controllable Synthesis of Submillimeter Single-Crystal Monolayer Graphene Domains on Copper Foils by Suppressing Nucleation. *J. Am. Chem. Soc.* **2012**, *134*, 3627–3630.

(11) Li, J.; Wang, X.-Y.; Liu, X.-R.; Jin, Z.; Wang, D.; Wan, L.-J. Facile Growth of Centimeter-Sized Single-Crystal Graphene on Copper Foil at Atmospheric Pressure. *J. Mater. Chem. C* **2015**, *3*, 3530–3535.

(12) Kraus, J.; Böbel, M.; Günther, S. Suppressing Graphene Nucleation during CVD on Polycrystalline Cu by Controlling the Content of the Support Foils. *Carbon* **2016**, *96*, 153–165.

(13) Li, X.; Magnuson, C. W.; Venugopal, A.; Tromp, R. M.; Hannon, J. B.; Vogel, E. M.; Colombo, L.; Ruoff, R. S. Large-Area Graphene Single Crystals Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper. *J. Am. Chem. Soc.* **2011**, *133*, 2816–2819.

(14) Chen, S.; Ji, H.; Chou, H.; Li, Q.; Li, H.; Suk, J. W.; Piner, R.; Liao, L.; Cai, W.; Ruoff, R. S. Millimeter-Size Single-Crystal Graphene by Suppressing Evaporative Loss of Cu During Low Pressure Chemical Vapor Deposition. *Adv. Mater.* **2013**, *25*, 2062–2065.

(15) Zhang, Y.; Zhang, L.; Kim, P.; Ge, M.; Li, Z.; Zhou, C. Vapor Trapping Growth of Single-Crystalline Graphene Flowers: Synthesis, Morphology, and Electronic Properties. *Nano Lett.* **2012**, *12*, 2810– 2816.

(16) Rümmeli, M. H.; Gorantla, S.; Bachmatiuk, A.; Phieler, J.; Geißler, N.; Ibrahim, I.; Pang, J.; Eckert, J. On the Role of Vapor Trapping for Chemical Vapor Deposition (CVD) Grown Graphene over Copper. *Chem. Mater.* **2013**, *25*, 4861–4866.

(17) Wang, C.; Chen, W.; Han, C.; Wang, G.; Tang, B.; Tang, C.; Wang, Y.; Zou, W.; Chen, W.; Zhang, X.-A.; Qin, S.; Chang, S.; Wang, L. Growth of Millimeter-Size Single Crystal Graphene on Cu Foils by Circumfluence Chemical Vapor Deposition. *Sci. Rep.* **2014**, *4*, 4537.

(18) Song, Y.; Pan, D.; Cheng, Y.; Wang, P.; Zhao, P.; Wang, H. Growth of Large Graphene Single Crystal Inside a Restricted Chamber by Chemical Vapor Deposition. *Carbon* **2015**, *95*, 1027–1032.

(19) Chen, C.-C.; Kuo, C.-J.; Liao, C.-D.; Chang, C.-F.; Tseng, C.-A.; Liu, C.-R.; Chen, Y.-T. Growth of Large-Area Graphene Single Crystals in Confined Reaction Space with Diffusion-Driven Chemical Vapor Deposition. *Chem. Mater.* **2015**, *27*, 6249–6258.

(20) Li, X.; Magnuson, C. W.; Venugopal, A.; An, J.; Suk, J. W.; Han, B.; Borysiak, M.; Cai, W.; Velamakanni, A.; Zhu, Y.; Fu, L.; Vogel, E. M.; Voelkl, E.; Colombo, L.; Ruoff, R. S. Graphene Films with Large Domain Size by a Two-Step Chemical Vapor Deposition Process. *Nano Lett.* **2010**, *10*, 4328–4334.

(21) Kim, H.; Mattevi, C.; Calvo, M. R.; Oberg, J. C.; Artiglia, L.; Agnoli, S.; Hirjibehedin, C. F.; Chhowalla, M.; Saiz, E. Activation Energy Paths for Graphene Nucleation and Growth on Cu. *ACS Nano* **2012**, *6*, 3614–3623.

(22) Zhou, H.; Yu, W. J.; Liu, L.; Cheng, R.; Chen, Y.; Huang, X.; Liu, Y.; Wang, Y.; Huang, Y.; Duan, X. Chemical Vapour Deposition Growth of Large Single Crystals of Monolayer and Bilayer Graphene. *Nat. Commun.* **2013**, *4*, 2096.

(23) Jacobberger, R. M.; Arnold, M. S. Graphene Growth Dynamics on Epitaxial Copper Thin Films. *Chem. Mater.* **2013**, *25*, 871–877.

(24) Gan, L.; Luo, Z. Turning off Hydrogen To Realize Seeded Growth of Subcentimeter Single-Crystal Graphene Grains on Copper. *ACS Nano* **2013**, *7*, 9480–9488.

(25) Eres, G.; Regmi, M.; Rouleau, C. M.; Chen, J.; Ivanov, I. N.; Puretzky, A. A.; Geohegan, D. B. Cooperative Island Growth of Large-Area Single-Crystal Graphene on Copper Using Chemical Vapor Deposition. *ACS Nano* **2014**, *8*, 5657–5669.

(26) Wang, S.; Hibino, H.; Suzuki, S.; Yamamoto, H. Atmospheric Pressure Chemical Vapor Deposition Growth of Millimeter-Scale Single-Crystalline Graphene on the Copper Surface with a Native Oxide Layer. *Chem. Mater.* **2016**, *28*, 4893–4900.

(27) Lin, L.; Li, J.; Ren, H.; Koh, A. L.; Kang, N.; Peng, H.; Xu, H. Q.; Liu, Z. Surface Engineering of Copper Foils for Growing Centimeter-Sized Single-Crystalline Graphene. *ACS Nano* **2016**, *10*, 2922–2929.

(28) Han, G. H.; Günes, F.; Bae, J. J.; Kim, E. S.; Chae, S. J.; Shin, H.-J.; Choi, J.-Y.; Pribat, D.; Lee, Y. H. Influence of Copper Morphology in Forming Nucleation Seeds for Graphene Growth. *Nano Lett.* **2011**, *11*, 4144–4148.

(29) Ago, H.; Kawahara, K.; Ogawa, Y.; Tanoue, S.; Bissett, M. A.; Tsuji, M.; Sakaguchi, H.; Koch, R. J.; Fromm, F.; Seyller, T.; Komatsu, K.; Tsukagoshi, K. Epitaxial Growth and Electronic Properties of Large Hexagonal Graphene Domains on Cu(111) Thin Film. *Appl. Phys. Express* **2013**, *6*, 075101.

(30) Ago, H.; Ohta, Y.; Hibino, H.; Yoshimura, D.; Takizawa, R.; Uchida, Y.; Tsuji, M.; Okajima, T.; Mitani, H.; Mizuno, S. Growth Dynamics of Single-Layer Graphene on Epitaxial Cu Surfaces. *Chem. Mater.* **2015**, *27*, 5377–5385.

(31) Miller, D. L.; Keller, M. W.; Shaw, J. M.; Rice, K. P.; Keller, R. R.; Diederichsen, K. M. Giant Secondary Grain Growth in Cu Films on Sapphire. *AIP Adv.* **2013**, *3*, 082105.

(32) Levendorf, M.; Ruiz-Vargas, C.; Garg, S.; Park, J. Transfer-Free Batch Fabrication of Single Layer Graphene Transistors. *Nano Lett.* **2009**, *9*, 4479–4483.

(33) Liu, N.; Pan, Z.; Fu, L.; Zhang, C.; Dai, B.; Liu, Z. The Origin of Wrinkles on Transferred Graphene. *Nano Res.* **2011**, *4*, 996–1004.

(34) Fang, W.; Hsu, A. L.; Song, Y.; Birdwell, A. G.; Amani, M.; Dubey, M.; Dresselhaus, M. S.; Palacios, T.; Kong, J. Asymmetric Growth of Bilayer Graphene on Copper Enclosures Using Low-Pressure Chemical Vapor Deposition. *ACS Nano* **2014**, *8*, 6491–6499. (35) Lee, A. L.; Tao, L.; Akinwande, D. Suppression of Copper Thin Film Loss during Graphene Synthesis. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1527–1532.

(36) Ismach, A.; Druzgalski, C.; Penwell, S.; Schwartzberg, A.; Zheng, M.; Javey, A.; Bokor, J.; Zhang, Y. Direct Chemical Vapor Deposition of Graphene on Dielectric Surfaces. *Nano Lett.* **2010**, *10*, 1542–1548.

(37) Howsare, C.; Weng, X.; Bojan, V.; Snyder, D.; Robinson, J. A. Substrate Considerations for Graphene Synthesis on Thin Copper Films. *Nanotechnology* **2012**, *23*, 135601.

(38) Tao, L.; Lee, J.; Chou, H.; Holt, M.; Ruoff, R. S.; Akinwande, D. Synthesis of High Quality Monolayer Graphene at Reduced Temperature on Hydrogen-Enriched Evaporated Copper (111) Films. ACS Nano 2012, 6, 2319–2325.

(39) Tao, L.; Lee, J.; Holt, M.; Chou, H.; McDonnell, S.; Ferrer, D.; Babenco, M.; Wallace, R.; Banerjee, S.; Ruoff, R.; Akinwande, D. Uniform Wafer-Scale Chemical Vapor Deposition of Graphene on Evaporated Cu (111) Film with Quality Comparable to Exfoliated Monolayer. J. Phys. Chem. C 2012, 116, 24068–24074.

(40) Jia, C.; Jiang, J.; Gan, L.; Guo, X. Direct Optical Characterization of Graphene Growth and Domains on Growth Substrates. *Sci. Rep.* **2012**, *2*, 707.

(41) Hu, T.; Zhang, Q.; Wells, J. C.; Gong, X.; Zhang, Z. A Comparative First-Principles Study of the Adsorption of a Carbon Atom on Copper and Nickel Surfaces. *Phys. Lett. A* **2010**, *374*, 4563–4567.

(42) Gajewski, G.; Pao, C.-W. Ab initio Calculations of the Reaction Pathways for Methane Decomposition over the Cu(111) Surface. *J. Chem. Phys.* **2011**, *135*, 064707.

(43) Jung, D. H.; Kang, C.; Nam, J. E.; Jeong, H.; Lee, J. S. Surface Diffusion Directed Growth of Anisotropic Graphene Domains on Different Copper Lattices. *Sci. Rep.* **2016**, *6*, 21136.

(44) Yu, Q.; et al. Control and Characterization of Individual Grains and Grain Boundaries in Graphene Grown by Chemical Vapour Deposition. *Nat. Mater.* **2011**, *10*, 443–449.

(45) Vlassiouk, I.; Regmi, M.; Fulvio, P.; Dai, S.; Datskos, P.; Eres, G.; Smirnov, S. Role of Hydrogen in Chemical Vapor Deposition Growth of Large Single-Crystal Graphene. *ACS Nano* **2011**, *5*, 6069–6076.

(46) Bhaviripudi, S.; Jia, X.; Dresselhaus, M. S.; Kong, J. Role of Kinetic Factors in Chemical Vapor Deposition Synthesis of Uniform Large Area Graphene Using Copper Catalyst. *Nano Lett.* **2010**, *10*, 4128–4133.

(47) Magnuson, C. W.; Kong, X.; Ji, H.; Tan, C.; Li, H.; Piner, R.; Ventrice, C. A. J.; Ruoff, R. S. Copper Oxide as a Self-Cleaning Substrate for Graphene Growth. J. Mater. Res. **2014**, *29*, 403–409.

(48) Kidambi, P. R.; Ducati, C.; Dlubak, B.; Gardiner, D.; Weatherup, R. S.; Martin, M.-B.; Seneor, P.; Coles, H.; Hofmann, S. The Parameter Space of Graphene Chemical Vapor Deposition on Polycrystalline Cu. J. Phys. Chem. C 2012, 116, 22492–22501.

(49) Davis, J. R. Copper and Copper Alloys; ASM Specialty Handbook; ASM International, 2001.

(50) Malard, L.; Pimenta, M.; Dresselhaus, G.; Dresselhaus, M. Raman Spectroscopy in Graphene. *Phys. Rep.* **2009**, 473, 51–87.

(51) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, *97*, 187401.

(52) Ferrari, A. C.; Basko, D. M. Raman Spectroscopy as a Versatile Tool for Studying the Properties of Graphene. *Nat. Nanotechnol.* **2013**, *8*, 235–246.