The Parameter Space of Graphene Chemical Vapor Deposition on Polycrystalline Cu

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Supporting Information

ABSTRACT: A systematic study of the parameter space of graphene chemical vapor deposition (CVD) on polycrystalline Cu foils is presented, aiming at a more fundamental process rationale in particular regarding the choice of carbon precursor and mitigation of Cu sublimation. CH₄ as precursor requires H₂ dilution and temperatures ≥1000 °C to keep the Cu surface reduced and yield a high-quality, complete monolayer graphene coverage. The H₂ atmosphere etches as-grown graphene; hence, maintaining a balanced CH₄/H₂ ratio is critical. Such balance is more easily achieved at low-pressure conditions, at which however Cu sublimation reaches deleterious levels. In contrast, C₆H₆ as precursor requires no reactive diluent and consistently gives similar graphene quality at 100−150 °C lower temperatures. The lower process temperature and more robust processing conditions allow the problem of Cu sublimation to be effectively addressed. Graphene formation is not inherently self-limited to a monolayer for any of the precursors. Rather, the higher the supplied carbon chemical potential, the higher the likelihood of film inhomogeneity and primary and secondary multilayer graphene nucleation. For the latter, domain boundaries of the inherently polycrystalline CVD graphene offer pathways for a continued carbon supply to the catalyst. Graphene formation is significantly affected by the Cu crystallography; i.e., the evolution of microstructure and texture of the catalyst template form an integral part of the CVD process.

INTRODUCTION

Economic, large-area growth combined with viable front and back-end integration strategies of monolayer and few-layer graphene (M/FLG) are key requirements for the commercial exploitation of graphene’s unique properties. Chemical vapor deposition (CVD) is the most promising route toward M/FLG production and integration, based on its versatility and success with other nanomaterials.¹⁻³ While progress has been made in achieving MLG CVD over large areas,⁴⁻⁻¹² the underlying growth mechanisms have yet to be fully understood⁴⁻⁻⁸ and the often narrow empirical process optimizations allow little generalization due to the vast CVD parameter space.⁴⁻⁻¹³ Most current literature focuses on exposing polycrystalline Cu⁴⁻⁻¹³ foils to methane (CH₄) at low pressures (LPs) and high temperatures (≥1000 °C). As-grown graphene can be fully continuous, but is inherently polycrystalline,¹⁰ with MLG domain sizes typically ≤5 μm in dimension.¹⁰⁻¹² Recent efforts have focused on increasing the MLG domain size,¹²⁻¹³ but in general the compromise made to achieve high-quality CVD graphene is to face undesirably high levels of Cu sublimation.¹⁴ Here, we focus on understanding graphene formation on polycrystalline Cu foils via a systematic exploration of the wider CVD parameter space, in particular regarding the choice of carbon precursor and mitigation of Cu sublimation, aiming at more rational process design. For CH₄ as precursor we find that, in agreement with previous literature,⁴⁻⁻¹³ uniform, high-quality MLG growth is restricted to a rather narrow CVD parameter set of LP conditions, H₂ dilution, and temperatures ≥1000 °C, at which Cu sublimation is at deleterious levels. The H₂ atmosphere is required to keep the Cu surface reduced, but...
at the same time can etch as-grown graphene. Hence, maintaining a balanced CH₄/H₂ ratio is critical, which makes the CH₄-based CVD process so delicate. In contrast, we find that benzene (C₆H₆) as precursor requires no reactive diluent, i.e., no delicate balance to be maintained, and consistently gives similar graphene quality at 100–150 °C lower temperatures compared to CH₄-based CVD. The lower process temperature and more robust processing conditions allow the problem of Cu sublimation to be effectively addressed. Our growth study shows that Cu-catalyzed CVD graphene formation is not inherently self-limited to a monolayer. Rather, we find the nucleation density, percentage of multilayer nuclei, and film uniformity/quality to critically depend on CVD conditions and growth kinetics. We suggest that the domain boundaries and other defects of the inherently polycrystalline CVD graphene offer pathways for the precursor to reach the catalyst even after complete MLG coverage. Our data further emphasize that the Cu catalyst template is not static and that the involved kinetics of grain growth are highly process dependent, making this an important process step for controlled graphene CVD.

### EXPERIMENTAL METHODS

Graphene synthesis is carried out in a customized cold-wall, low-pressure CVD (LPCVD) reactor (a heavily modified Aixtron BM3, base pressure ~5 × 10⁻⁶ mbar) and a hot-wall, atmospheric-pressure furnace (APCVD). For LPCVD the total pressure (0.001–100 mbar) was regulated by a pressure controller at the reactor outlet. Commercial, cold-rolled Cu foils of different thicknesses and purities (Alfa Aesar Puratronic, 99.999% purity, 25 and 100 μm thick; Advent Research Materials, 99.995% purity, 12 μm thick) are used as catalysts. A one-step CVD recipe is used as a benchmark process for all systems. For all CVD recipes, heating and preannealing is carried out in H₂ at 1000 °C (LPCVD, 4 mbar total pressure, heating rate ~250 °C/min to 800 °C followed by 50 °C/min to 1000 °C; APCVD, heating rate ~40 °C/min), after which the temperature is stabilized at the chosen growth temperature. In the case of CH₄ as the precursor, CH₄ is added to the annealing gas and cooling is performed in pure Ar (LPCVD cooling ramp ~150 °C/min to 400 °C at 7 mbar, APCVD cooling rate ~30 °C/min). For C₆H₆ LPCVD, the exposure is to C₆H₆ (>99.7% purity, Sigma-Aldrich) without H₂ and cooling is performed in a vacuum.

Samples were characterized by scanning electron microscopy (SEM; Philips XL30, 1–2 kV) and Raman spectroscopy (Renishaw InVia spectrometer, 532 nm excitation). For the latter the M/FLG was typically transferred to SiO₂ (300 nm)/Si substrates using a poly(methyl methacrylate) (PMMA) support layer and a 0.5 M aqueous solution of FeCl₃ to etch the Cu foil. Acetone was then used to dissolve the PMMA support. Hall-bar devices were fabricated via e-beam lithography. Graphene layers, transferred to SiO₂/Si wafer substrates, were etched by an O₂ plasma and Au/Ti contacts evaporated on top. All electrical measurements were performed at room temperature. Electron backscattered diffraction (EBSD) experiments were performed in an FEI Helios dual-beam microscope (5–15 kV, current ~5.5 nA, working distance ~5–6.5 mm, and sample tilt of ~60° with respect to the electron beam) with an Oxford Instruments HKL EBSD Nordlys II detector in spot mode using Channel 5 software. Birefringence measurements followed the method outlined by Kim et al.¹⁵ Liquid crystals of 4-pentyl-4′-cyanobiphenyl (SCB; Merck GmbH) were drop cast onto graphene transferred to a glass substrate. A thin coverslip was added on top, and measurements were carried out with the as-prepared sample placed between two crossed polarizers on a rotatable stage.

## RESULTS

The process of graphene formation on metal surfaces in general comprises nucleation, a subsequent expansion of the nuclei into domains, followed by a merging of the domains into a continuous covalently bonded film.¹⁶ Here we refer to domains as regions that grow from a single nucleation point. Figure 1 shows SEM images of the Cu surface after short CH₄/H₂ exposures (see process details in the caption), i.e., the early stages of CVD before the graphene coverage is continuous. Clear differences can already be seen for the different CVD

![Figure 1. SEM images at different magnifications showing graphene nuclei on Cu before merging to form a continuous film: (a, b) monolayer nuclei, LPCVD, 4 mbar, 1000 °C, 1:10 CH₄/H₂ for 25 min, before merging to form a continuous film on 99.999% pure 25 μm foil, (c, d) multilayer nuclei, LPCVD, 4 mbar, 1000 °C, 1:1 CH₄/H₂ for 5 min, on 99.999% pure 100 μm foil, (e, f) multilayer nuclei, LPCVD, 4 mbar, 1000 °C, 1:1 CH₄/H₂, CH₄/H₂ for 5 min, on 99.999% pure 100 μm foil with the underlying Cu grain orientation measured by EBSD, (g, h) multilayer nuclei, APCVD, 1000 °C, 1:25 CH₄/H₂ for 5 min, on 99.999% pure 25 μm foil, (i, j) multilayer nuclei, APCVD, 1000 °C, 1:25 CH₄/H₂, CH₄/H₂ for 5 min, on 99.995% pure 12 μm Cu foil.](dx.doi.org/10.1021/jp303597m)
conditions. Parts a,b and parts c,d of Figure 1 compare low (1:10) and high (1:1) CH\textsubscript{4}/H\textsubscript{2} ratios for LPCVD conditions. For the former we observe MLG domains ranging from typically \(\sim 30\) to \(40\) \(\mu\text{m}^2\) in size, with a few isolated areas (2–4 \(\mu\text{m}^2\)) of FLG (as seen by SEM contrast and confirmed by Raman spectroscopy; see below). This is largely consistent with recent literature on optimized CVD with CH\textsubscript{4} on Cu foils.\textsuperscript{4,5,9–13} We note that, due to the pressure regulation and backfilling procedure, the CH\textsubscript{4}/H\textsubscript{2} ratio for our process is initially lower at the point of CH\textsubscript{4} addition and thus partly resembles two-step exposures reported in the literature.\textsuperscript{17} A higher CH\textsubscript{4} partial pressure (Figure 1c,d) leads to predominantly multilayer graphene nucleation and decreased sample homogeneity. This highlights that, at the initial stages of growth, which we refer to as the primary nucleation stage, Cu is not inherently limiting graphene formation to a monolayer.

Parts e–j of Figure 1 highlight that the nature of graphene nucleation and growth at the early stages is highly dependent on the catalyst surface orientation and impurity levels. Parts e,f of Figure 1 show that for the same CVD conditions the resultant graphene coverage is different on adjacent Cu facets, with the imaged Cu(111) surface showing less graphene coverage compared to the Cu(110) surface. APCVD conditions as in Figure 1g–j result in a predominantly multilayer nucleation pattern. The nucleation density is notably increased and the shape of the nuclei significantly changed for a Cu foil of lower purity (Figure 1i,j) at otherwise identical APCVD conditions. The FLG nuclei preferentially decorate Cu grain boundaries and appear aligned along the rolling striations of the foil. We find that a variation from 25 to 100 \(\mu\text{m}\) in foil thickness does not appear to influence the kinetics of graphene formation on that scale (Figure 1c–f), but the foil thickness does influence the Cu grain growth kinetics as discussed below.

Figure 2 shows the results of EBSD analysis marked across SEM images of Cu foil surfaces for various process stages and conditions, highlighting the effects of Cu recrystallization and grain growth. Rolling striations are a dominant feature of the as-received Cu foils, for which EBSD shows Cu grain sizes <2 \(\mu\text{m}\) with diverse surface orientations (Figure 2a; Table S1, Supporting Information). We find the detailed deformation texture of the used commercial cold-rolled Cu foils to vary, despite being advertised as the same product. Hence, the starting point cannot be automatically assumed as constant. It should be noted that here we do not use any additional Cu surface treatment procedure, such as electropolishing.\textsuperscript{18} After annealing in H\textsubscript{2} at 1000 °C, the Cu grain sizes increase to \(\sim 50–500\) \(\mu\text{m}\) for APCVD and \(\sim 50\) \(\mu\text{m}–2\) mm for LPCVD conditions (Figure 2b,c), which exceed the foil thickness. While for APCVD we still find a crystallographically diverse Cu surface (Figure 2b), the texture after LPCVD annealing becomes (111)-dominated (Figure 2c). The surface topography appears rougher and stepped for LPCVD conditions (Figure 2c inset, with individual step heights of \(\sim 10–50\) nm) compared to the relatively smooth surface seen for APCVD conditions. The Cu grain size and orientation distributions are similar before and after hydrocarbon exposure (Figure 2d,e); most notably, a (111)-dominated texture for LPCVD conditions is maintained and several orientations are seen for APCVD. A polycrystalline material has no equilibrium structure, but depending on processing reaches a metastable equilibrium where the total grain boundary energy is locally minimized. At the given conditions, recrystallization followed by normal and abnormal grain growth is expected,\textsuperscript{19} and Figure 2 is consistent with that.

![Figure 2](image_url)

Our data emphasize that the Cu catalyst template is not static and that the involved kinetics of grain growth are highly process dependent, making this an important process step for controlled graphene CVD.

We note that most literature directed toward the optimization of uniform MLG CVD focuses on low-pressure conditions in the millibar range,\textsuperscript{17} during H\textsubscript{2} pretreatment and CH\textsubscript{4}/H\textsubscript{2} exposure, similar to our LPCVD conditions of Figures 1a,b and 2e. On the basis of their prevalence, we choose these LPCVD conditions as the standard “reference” for our further parametric study. Our discussion below will highlight why achieving continuous MLG films based on APCVD is challenging using CH\textsubscript{4} as the precursor. Figure 3 highlights the quality of graphene grown at our reference CH\textsubscript{4}-based LPCVD conditions. Figure 3a shows an optical image of as-grown MLG transferred to a SiO\textsubscript{2} (300 nm)/Si substrate. A corresponding Raman spectrum in Figure 3b with G (\(\approx 1600\) cm\textsuperscript{−1}, fwhm \(\approx 23–25\) cm\textsuperscript{−1}), D (\(\approx 1360\) cm\textsuperscript{−1}), and 2D (\(\approx 2700\) cm\textsuperscript{−1}) peaks visible. The Journal of Physical Chemistry C
Kim et al.15 Parts h and i of Figure 3 show polarizing optical microscopy technique as recently reported by larger areas, we validate the potential of a liquid crystal based devices (Figure 3g) give sheet resistances (on a SiO2 support) and (f) show the corresponding distribution statistics. (g) Six contact Hall geometry devices. (h) Control POM image in a region of the sample containing no graphene. (i) POM image for a liquid crystal (LC) over graphene sample.

Figure 3. Characterization of a large-area MLG film grown in LPCVD, 4 mbar, 1000 °C, 1:5 CH4/H2 for 30 min, on 99.999% pure 25 μm foil: (a) optical image, (b) Raman spectrum confirming the presence of MLG. Raman map of large-area MLG (c) I2D/I_G and (e) I_D/I_G. (d) and (f) show the corresponding distribution statistics. (g) Six contact Hall geometry devices. (h) Control POM image in a region of the sample containing no graphene. (i) POM image for a liquid crystal (LC) over graphene sample.

cm−1, fwhm ≈ 35−37 cm−1, which can be fitted with a single Lorentzian function) peaks as well as an I2D/I_G ratio of ≈3.5 and I_D/I_G ratio of ≈0.05 demonstrate the high quality of the MLG.26,31 Parts c and e of Figure 3 show Raman I2D/I_G and I_D/I_G maps of the MLG (dimensions 50 μm × 50 μm), respectively, along with the corresponding distribution statistics (Figure 3d,f). The maps show average values of I2D/I_G ≈ 3.5 and I_D/I_G ≈ 0.05 over a large area. Six contact Hall geometry devices (Figure 3g) give sheet resistances (on a SiO2 support) in the range of 400−800 Ω/□ and mobilities in the 2000−3000 cm2 V−1 s−1 range (with a p doping of a few 1012 cm−2).

To characterize sample uniformity and polycrystallinity over larger areas, we validate the potential of a liquid crystal based polarizing optical microscopy technique as recently reported by Kim et al.15 Parts h and i of Figure 3 show polarizing optical microscopy (POM) images of an empty control and our reference MLG, respectively. The POM contrast is based on sample interactions with a SCB nematic liquid crystal (see the Supporting Information). Across a 1 cm2 MLG area, POM indicates feature sizes ranging from ~40 μm2 to a few hundred square micrometers, which is consistent with the observed nucleus sizes of ~30−40 μm2 in Figure 1 and the subsequent merging of domains with roughly similar orientations. We note that all characterization above is done after graphene transfer; i.e., it includes possible degradation incurred during transfer.

Whereas "optimized" CVD parameters can be highly system specific, we note that the variation of key parameters over a wide range offers fundamental insights into the growth process and allows the establishment of more generic growth guidelines. Figure 4 shows results of our systematic exploration of the wider CVD parameter space and focuses on the effects of total pressure, growth time, and hydrocarbon partial pressure, where for each experiment only one specified parameter was varied starting from the LPCVD benchmark recipe (see Figure 3). The results are presented in terms of optical images of as-grown graphene films transferred to SiO2 (300 nm)/Si (Figure 4a–f) and corresponding Raman spectra (Figure 4g). For a lower total pressure of 1 mbar only MLG and no FLG is observed, but for the given exposure the film has large holes (Figure 4a). This is indicative of a lower graphene nucleation density and growth rate. We note that rather than focusing only on the carbon precursor and carbon addition, also competing etching processes, e.g., by H2 or H2O, have to be considered.21,22 We clearly observe that as-grown graphene on Cu is etched while annealing in a H2 atmosphere, which is the main reason why we do not use hydrogen during cooldown, in contrast to other studies.23 We note that although this etching occurs in the presence of H2 (at sufficiently high partial pressures), it may also arise from residual water or oxygen contamination.8 A total pressure of 8 mbar on the other hand leads to a significant increase in FLG nucleation and film inhomogeneity. An analogous behavior is seen for an increase in the CH4 partial pressure (Figures 3a and 4e,f), where 1:10 CH4/H2 results in incomplete MLG coverage and a 1:1 ratio shows significant multilayer coverage. In general, the lower the carbon precursor pressure, the lower the likelihood of achieving complete MLG surface coverage.

Parts c and d of Figure 4 combined with the reference sample in Figure 3a show the effect of growth time: the longer the growth time, the more complete the graphene coverage. Extended exposures, however, increase the fractional multilayer coverage. Importantly, we find that new graphene layers can nucleate after the completion of a monolayer. We refer to this as secondary nucleation, as compared to the primary nucleation discussed above. In this context, we note that in Figure 4b,d,f the nucleation pattern of multilayered graphene appears to follow the rolling striations of the Cu foil. Figure 4g shows that the interpretation of optical contrast in Figure 4a–f is in full agreement with measured Raman spectra corresponding to monolayer (I2D/I_G > 2), and bilayer (I2D/I_G ≈ 1) and multilayer (I2D/I_G < 1) graphene. Furthermore, the Raman measurements in Figure 4g also confirm the interpretation of SEM contrast regarding multilayer graphene primary nucleation for APCVD conditions in Figure 1e–h. The bilayer and FLG seen in areas of Figure 4d–f show Raman spectra (Figure 4g) corresponding to turbostratic graphene with 2D peaks that can be fitted with single Lorentzian peaks, whereas the APCVD conditions show a Raman signature consistent with Bernal stacking.20
Figure 5 shows the results of LPCVD in undiluted CH$_4$ to assess the role of hydrogen dilution during growth in more detail. The postgrowth Cu surface is dominated by triangular and other three lobed structures (Figure 5a−d), partly resembling a Sierpinski triangle like fractal pattern. An EBSD analysis (Figure 2f) shows a predominant (111) texture for the processed Cu foil, whereby the triangles and lobed structures formed on Cu(111) facets and are not present on Cu(001). Attempts to transfer the structures to SiO$_2$/Si substrates resulted in small discontinuous patches of graphene and residual PMMA. Raman confirms the transferred patches as MLG (Figure 5f). Importantly, Raman spectra (457 nm excitation) measured directly on the processed Cu foil show peaks corresponding to CuO (300 and 652 cm$^{-1}$) and CuO$_2$ (217, 415, 504, and 808 cm$^{-1}$) for the triangular areas. The mechanisms of this self-organization are unclear, but we suggest it arises on the basis of the balance of three competing processes, namely, graphene formation, its etching by residual oxygen, and the formation of copper oxide from this residual oxygen. The parallel processes of reduction and oxidation could make the copper oxide species extremely mobile, causing them to self-align in a triangular fashion due to the 3-fold symmetry of Cu(111). Hence, our data show that the presence of a hydrogen atmosphere suppresses the formation of copper oxide from trace oxygen contamination during CVD. We note that the observation of triangular graphene on Cu(111) has been reported in recent literature, without however considering the role of oxygen. This highlights why CH$_4$ as precursor requires H$_2$ dilution, and our data above emphasize the delicate effects of the CH$_4$/H$_2$ balance.

Figure 5h shows that for LPCVD conditions at 1000 °C the rate of Cu sublimation is significant and deleterious. Increasing
the total pressure with an inert diluent can suppress the Cu sublimation, but as discussed below, maintaining the CH4/H2 balance and achieving complete MLG coverage then becomes increasingly challenging.28 The exponential variation of vapor pressure with temperature strongly motivates a temperature reduction to mitigate the Cu sublimation. Parts a−d of Figure 6 show the effect of lowering the process temperature for CH4-based graphene CVD on Cu. Comparing graphitic films grown at 1000, 900, and 800 °C, the optical images of the transferred films all appear homogeneous (Figure 6a−c). The corresponding Raman spectra, however, show a significant deterioration in graphene quality, as highlighted by the significantly increased D peak intensity. The spectrum for 900 °C shows an I2D/I_G ratio of ∼2.5 and I_D/I_G ratio of ∼0.35. Also observed is the emergence of an additional defect peak, referred to as the D′ peak,29 near the G peak at higher wavenumbers. A further reduction in temperature to 800 °C leads to I2D/I_G ≈ 1.2 and I_D/I_G ≈ 0.79 and a D′ peak intensity increased to the level of I_G. We also note that all these films are continuous, in contrast to recent literature that claims that no continuous films can be obtained below 1000 °C at comparable experimental conditions.33 Whereas the parameters discussed in Figure 4 mainly influence the M/FLG ratio and coverage, the growth temperature is clearly the most significant parameter influencing the crystalline quality of the as-grown material. Our data show that with CH4 as precursor the growth temperature cannot be lowered sufficiently to mitigate Cu sublimation and at the same time maintain a high graphene quality.

This raises the question of what fundamentally determines at how low a temperature high-quality graphene CVD can be grown. We approach this question here by using benzene (C6H6) as an alternative carbon precursor. Figure 6e shows the results of LPCVD, for which a simple exposure to undiluted C6H6 was adopted. At 900 °C, highly uniform MLG films of high quality (I_D/I_G ≈ 0.06, Figure 6e) are achieved with greatly reduced Cu sublimation compared to 1000 °C. As in Figure 6d, the graphene quality decreases with decreasing growth temperature (Figure 6e). However, the MLG quality for...
C₆H₆-based CVD is better at any given temperature (compare parts d and e of Figure 6), and unlike for CH₄, graphitic material (albeit highly defective) nucleates at temperatures as low as 600 °C for C₆H₆. Figure 6f directly compares the measured I_D/I_G ratios for the two different carbon precursors. Raman maps for the C₆H₆-derived MLG at 900 °C show a uniform I_D/I_G ≈ 0.06 and I_G/I_G ≈ 2.5 distribution over a large area (dimensions 50 μm × 50 μm) as seen in Figure 7a–d. POM indicates a similar grain size distribution and polycrystallinity for the C₆H₆-derived MLG films (Figure 7i,j) as compared to the reference samples for CH₄/H₂-based CVD (Figure 3b,i). Furthermore, six contact Hall geometry devices based on graphene grown from C₆H₆ at 900 °C give sheet resistances (on a SiO₂ support) in the range of 400–800 Ω/□ and mobilities in the 2000–3000 cm² V⁻¹ s⁻¹ range (with a p-doping of a few 10¹² cm⁻²). These results highlight that C₆H₆ enables similar graphene quality at 100–150 °C lower temperatures, i.e., that the apparent low-temperature limit is precursor dependent.

The variation of CVD parameters over a wider parameter space for the benzene-based process shows a similar general behavior compared to that with CH₄ as precursor (Figure 7e–h). In particular, the lower the carbon precursor partial pressure, the lower the likelihood of achieving complete MLG surface coverage, and the higher the exposure pressure, the higher the likelihood of multilayer nucleation and film inhomogeneity. Again, the growth rate depends on the specific Cu surface. However, considering that between parts e and f and parts g and h of Figure 7 the C₆H₆ partial pressure increase was ~100-fold, the increase in fractional FLG coverage and inhomogeneity is surprisingly little. Significantly, we note that the partial pressure range in which C₆H₆ yields MLG (∼10⁻⁴–10⁻² mbar) is much wider (relative to the partial pressure used) than for the CH₄ process (∼0.2–1.5 mbar). Hence, for the conditions used, C₆H₆ as precursor does not require H₂ dilution and enables growth at lower temperatures with more robust processing conditions.

**Discussion**

The overall CVD process for graphene growth can be discussed in the context of basic heterogeneous catalysis and 2D crystal growth kinetics as a multistep reaction comprising (1) gaseous precursor transport to and dissociation on the catalyst surface, (2) transport of carbon (species) on the surface and into/out of the bulk of the catalyst, (3) graphene nucleation and carbon incorporation into the growing graphene layer, and (4) etching of the as-formed graphene. Step 1 thereby comprises transport of gas reactants through the boundary layer above the catalyst surface and the adsorption/desorption kinetics of the catalytic reaction. Simultaneous to its formation, graphene etching can occur (step 4), depending on the composition of the gas atmosphere and the presence of contaminants in the CVD setup/process. The thermodynamic driving force for growth, i.e., step 3, is a carbon supersaturation at the catalyst surface.

In CVD this supersaturation is created via step 1, whereby the different CVD conditions can be expressed as different carbon chemical potentials. The chemical potential depends on the temperature and partial pressures, which in turn depend on the choice of precursor and the reaction considered. A more reactive carbon source corresponds to carbon supplied at a higher chemical potential. We adopt this general framework here to qualitatively rationalize our findings, even though the experimental conditions might not be close to equilibrium; i.e., the carbon chemical potential is difficult to quantify.

For carbon supplied at a very high chemical potential, graphene growth is very favorable and can become nonspecific to details of the catalyst surface. Our data here (Figures 1, 4, and 7) are consistent with such a generic behavior insofar that the higher the supplied carbon chemical potential, the higher the likelihood of film inhomogeneity and primary and secondary multilayer nucleation. Assuming growth occurs isothermally during CVD exposure and not during cooldown and that additional layers grow in contact with the catalyst, i.e.,
underneath the existing graphene\textsuperscript{33,32} secondary nucleation indicates that carbon reaches the Cu surface even after complete MLG coverage. Isolated graphene flakes have been shown to be impermeable to gases\textsuperscript{33} hence, we suggest that the observed carbon leakage is due to the inherent polycrystallinity of as-grown MLG whereby the domain boundaries and other defects offer pathways for the precursor to reach the catalyst. Hence, clearly graphene CVD on Cu cannot be expected to inherently (independent of the conditions applied) give a self-limiting homogeneous monolayer coverage. We emphasize that this has important ramifications for FLG CVD. Primary nucleation will not give a homogeneous FLG coverage due to the different growth rates of the layers. Secondary nucleation will require leakage through the covering layer(s), and the challenge is thereby to feed homogeneous growth through inhomogeneous leakage. Furthermore, we expect the leakage to significantly decrease with the number of layers, so the number of layers possible is clearly limited by this method.

The more the supplied carbon chemical potential is lowered, the more specific the graphene formation becomes to details of the catalyst surface, nature of nucleation sites, energy costs associated with graphene edges, and, for instance, additional strain energies depending on the lattice mismatch.\textsuperscript{30} Figures 1 and 7 highlight that graphene formation is indeed dependent on the catalyst surface orientation and impurity levels. Improved growth on Cu(111) has been previously attributed to improved precursor adsorption and high diffusion of carbon species.\textsuperscript{34} Compared to, for instance, Ni, Cu in its given metallic state is a less active catalyst for step 1; hence, higher temperatures are required to supply carbon at a given rate. Compared to CH\textsubscript{4}, C\textsubscript{6}H\textsubscript{6} represents a more reactive carbon source, which is captured in the temperature dependence of Figure 6. Hence, it is not surprising that we do not see any graphitic deposits at temperatures below 700 °C for CH\textsubscript{4} whereas for C\textsubscript{6}H\textsubscript{6} we observe carbon film deposition at temperatures as low as 300 °C (see Figure 6e) on Cu for the given conditions. Below 600 °C, the crystallinity of the as-grown carbon is poor, and although the defect density will again depend on the detailed growth kinetics (e.g., carbon arrival rate vs incorporation rate), we cannot reproduce the Cu-catalyzed growth of graphene at a temperature of 600 °C \textsuperscript{28} hence, we cannot reproduce the Cu-catalyzed growth of graphene at a temperature of 600 °C for CH\textsubscript{4} as recently reported for toluene\textsuperscript{18} the arrival rate vs incorporation rate), we cannot reproduce the Cu-catalyzed growth of graphene at a temperature of 600 °C \textsuperscript{28}. On the basis of our data, we suggest here that the delicate CH\textsubscript{4}/H\textsubscript{2} balance shifts for pressure-induced changes of the boundary layer, and this is why achieving continuous MLG films based on APCVD is very challenging using CH\textsubscript{4} as precursor. C\textsubscript{6}H\textsubscript{6} as precursor on the other hand is more reactive and requires no reactive diluent and related delicate balancing. We also suggest that diluting C\textsubscript{6}H\textsubscript{6} with a neutral gas such as Ar should be much more straightforward than for CH\textsubscript{4} in terms of maintaining high-quality graphene growth.

The above argumentation assumes that the observed graphene formation on Cu occurs predominantly during the precursor exposure at isothermal conditions, rather than due to precipitation upon cooling.\textsuperscript{7,8} This assumption is supported by in situ observations of isothermal graphene growth on Cu during elemental carbon deposition;\textsuperscript{\textsuperscript{30}} however, the importance of the contribution of carbon precipitation on cooling should also be considered. On the basis of a simplistic consideration of carbon solubility in Cu at 1000 °C of between 0.00070 atom %\textsuperscript{39} and 0.028 atom %\textsuperscript{40}, the amount of carbon dissolved in the 25 μm foil corresponds to between 0.4 and 15.5 layers of graphene with an atomic density of 3.8 × 10\textsuperscript{19} carbon atoms m\textsuperscript{2}. It should be noted that the large uncertainties here reflect the significant disparities between the solubility values reported in the literature.\textsuperscript{39,40} Realistically, the diffusion lengths of carbon dissolution and precipitation may limit the active volume to some fraction of the foil thickness and should be considered when estimating whether the quantity of carbon that precipitates as graphene upon cooling is significant.\textsuperscript{8} For such a calculation to be informative, a validation of the solubility and diffusivity of carbon in Cu is required, which lies beyond the scope of the present work. We note that further in situ experiments are needed to fully clarify the relative importance of growth by precipitation upon cooling.

\section*{CONCLUSIONS}

We systematically explored the parameter space of graphene CVD on polycrystalline Cu foils in particular regarding the choice of carbon precursor and mitigation of Cu sublimation as required for industrial manufacture. CH\textsubscript{4} is the currently most widely used carbon precursor, requires H\textsubscript{2} dilution and high temperatures (1000 °C) to keep the Cu surface reduced and yield high-quality graphene. The H\textsubscript{2} atmosphere etches as-grown graphene; hence, maintaining a balanced CH\textsubscript{4}/H\textsubscript{2} ratio is critical. Such balance is more easily achieved at low-pressure conditions, at which however Cu sublimation is at deleterious levels. In contrast, C\textsubscript{6}H\textsubscript{6} as precursor requires no reactive dilution, i.e., no delicate balance to be maintained, and consistently gives similar graphene quality at 100–150 °C lower temperatures compared to CH\textsubscript{4}-based CVD. The lower process temperature and more robust processing conditions allow the problem of Cu sublimation to be effectively addressed. Our growth study shows that Cu is not inherently limiting graphene formation to a monolayer. Rather, the higher the supplied carbon chemical potential, the higher the likelihood of film inhomogeneity and primary and secondary
multilayer nucleation. Secondary nucleation indicates that carbon reaches the Cu surface even after complete MLG coverage, whereby we suggest that the domain boundaries of the inherently polycrystalline layers offer pathways for the precursor to reach the catalyst. Our data further emphasize that the Cu catalyst template is not static and that the involved kinetics of grain growth are highly process dependent, making this an important process step for controlled graphene CVD.

Although the data presented concern only two carbon precursors, we expect the insights achieved to be of general relevance for the optimization of graphene CVD and more rational process design. While C6H6 may not be the precursor of choice for industrial upscaling due to its harmful e

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