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Controlling Nucleation Density While Simultaneously Promoting Edge-Growth Using Oxygen-Assisted Fast Synthesis of Isolated Large-Domain Graphene

Phi H.Q. Pham†, Weiwei Zhou†, Nhi V. Quach†, Jinfeng Li†, Jian-Guo Zheng‡, Peter J. Burke†*

†Department of Electrical Engineering and Computer Science, University of California, Irvine, CA 92697, USA

‡Irvine Materials Research Institute University of California Irvine, CA 92697, USA

ABSTRACT

We report a two-step chemical vapor deposition (CVD) growth method for rapid synthesis of isolated large-domain graphene. The key feature of the two-step growth method is to separate nucleation from growth, performing the nucleation in step-one with a low carbon feedstock (methane) gas flow rate, and rapid growth in step-two with a high flow rate. We find empirically that, even under the high flow rate conditions of step-two, the nucleation density on the inside of the copper pocket used for growth is suppressed (preventing merging of domains into full films) until the graphene growing on the outside of the pocket merges into a full film, fully covering the outside. The mechanism for this suppression is believed to be related to oxygen-assisted passivation of nucleation sites, a decreased energetic barrier for edge-attachment growth, and diffusion of carbon through the copper bulk. These conditions enable us to finely tune the local carbon concentration on the inside surface for fast growth and minimum nucleation density, and achieve a growth of 5-mm isolated graphene domains in under 5 hours of total growth time, much faster than traditional one-step growth methods.

INTRODUCTION

What is the most rapid, efficient chemical vapor deposition (CVD) method to produce large-area, single-domain graphene? This task remains a challenge because rapid growth conditions usually result in concomitant high nucleation density, causing merging of domains and ultimately, full film coverage[1–3], prior to the growth of large domains. This results in multiple, detrimental grain boundaries[4] due to the polycrystalline nature of multi-domain films[5]. The ultimate goal, and only way to ensure that no grain boundaries exist within the graphene is the synthesis of wafer-scale, isolated single-domains. En route to reaching this goal, researchers have developed numerous methods (such as electropolishing copper foils[6], high pressure hydrogen annealing[7], low methane flow[2], and oxidized copper growth[8,9]) to minimize the nucleation density. Of these, CVD growth on oxidized copper substrates has proven to be one of the most effective[8,9] at allowing the necessary surface-area and spacing required to avoid merging of neighboring domains. However, this method, which relies on low flow rates of the carbon feedstock gas, comes at the cost of very long growth times[8–12], measured in days instead of hours.

Here, we report a two-step CVD growth method for rapid synthesis of isolated large-domain graphene. The key feature of the two-step growth method is to separate nucleation from growth, performing the nucleation in step-one with a low feedstock gas (methane) flow rate, and rapid growth in step-two with a high flow rate. We find empirically that, even under the high flow rate conditions of step-two, the nucleation density is suppressed by the geometry of the copper pocket[6] used, until the outside of the copper pocket is fully covered by a graphene film. During step-two (the high growth rate step), we are able to tune the carbon concentration on the inside of the copper pocket to be *above* the threshold concentration required for edge growth, but *below*

the threshold concentration required for nucleation[13], even in the presence of high methane flow rates. Operating in this regime produces large-domain graphene without the formation of full films, ensuring that no detrimental grain boundaries develop.

A unique combination of mechanisms enables us to grow in this regime. While a quantitative model is still not available, the mechanisms involved are believed to include 1) passivation of active nucleation sites through oxidation of the copper surface[9], 2) reduction of the energy barrier for edge-attachment growth resulting from the de-hydrogenation of methane by the oxidized copper surface[8], and 3) a unique carbon concentration profile (resulting from the role of carbon sources and sinks at the inside and outside due to nucleation, growth, and diffusion of carbon through the copper bulk[14], in both directions). This "window" has not been explored previously in the literature. Furthermore, we show that this "window" of opportunity exists only when the outside is not fully covered with graphene. Once the outside surface is covered, the nucleation density on the inner surface increases dramatically, and quickly results in fully merged films with grain boundaries, rather than isolated single domains (the goal of this work). Using this approach, we demonstrate growth of 5-mm isolated graphene domains in less than 5 hours of total growth time, much faster than traditional one-step growth methods.

RESULTS

We performed CVD graphene growth using enclosed copper pockets due to the improved surface conditions and decreased diffusivity, and hence, decreased nucleation and growth rate in the interior surface as reported in previous CVD studies[2,6,14]. Our findings regarding diffusion from the inside surface to the outside surface of the copper pocket will be discussed in depth, later in the paper. Briefly, a copper pocket is used, and large-domains grow on the inside. Our studies show a critical role of the surface coverage of the outside surface influencing growth on

the inside, elucidated in detail below. Preparation of the enclosed copper pocket is documented in the methods and supporting information **(Fig. S1)**. Before growth optimization (two-step growth) experiments were conducted, we monitored and adjusted pre-growth conditions (excluding methane flow rate) to achieve the lowest nucleation density possible. These results including oxidation conditions[8,10], annealing conditions[7,9], and heating gases[11,12] are documented in (**Fig. S2)**. These parameters are held constant throughout the remainder of experiments including two-step growth studies **(Fig. S3)**.

Typically, for one-step growth procedures, a low methane flow rate is used over long durations in order to keep the nucleation density low[8–12]. This methodology to achieve low nucleation density comes at the cost that the growth rate is also low[8–12], especially since the growth rate decreases overtime[15]. As verified in **(Fig. S4a-b)**, when using a low methane flow rate (.4 sccm), distinct mm-sized domains appear in low density **(Fig. S5a-b)**, but long growth durations have limited effects on increasing domain size. To assess if a high methane flow rate could be used to synthesis large-domain graphene, we performed a series of one-step growths using elevated methane flow rates (1.6 sccm) to probe the domain-size and nucleation density overtime **(Fig. 1a)**. Following growth, the enclosed copper pockets are cut open, and oxidized on a hotplate to reveal graphene growth coverage[16]. **(Fig. 1b-d)** shows a depiction and experimental verification that using elevated methane flow rates can noticeably increase the graphene domain-size, but due to the increased nucleation density **(Fig. S5c-d)**, results in the formation of merged domains, and ultimately, continuous graphene films, as the growth duration proceeds. From these control studies, we confirm that in order to synthesize large-domain graphene using an increased methane flow rate (in order to decrease the overall growth duration), without the detriment of

increased nucleation density (which would limit the ultimate size of isolated graphene domains), a traditional one-step growth protocol is not adequate.

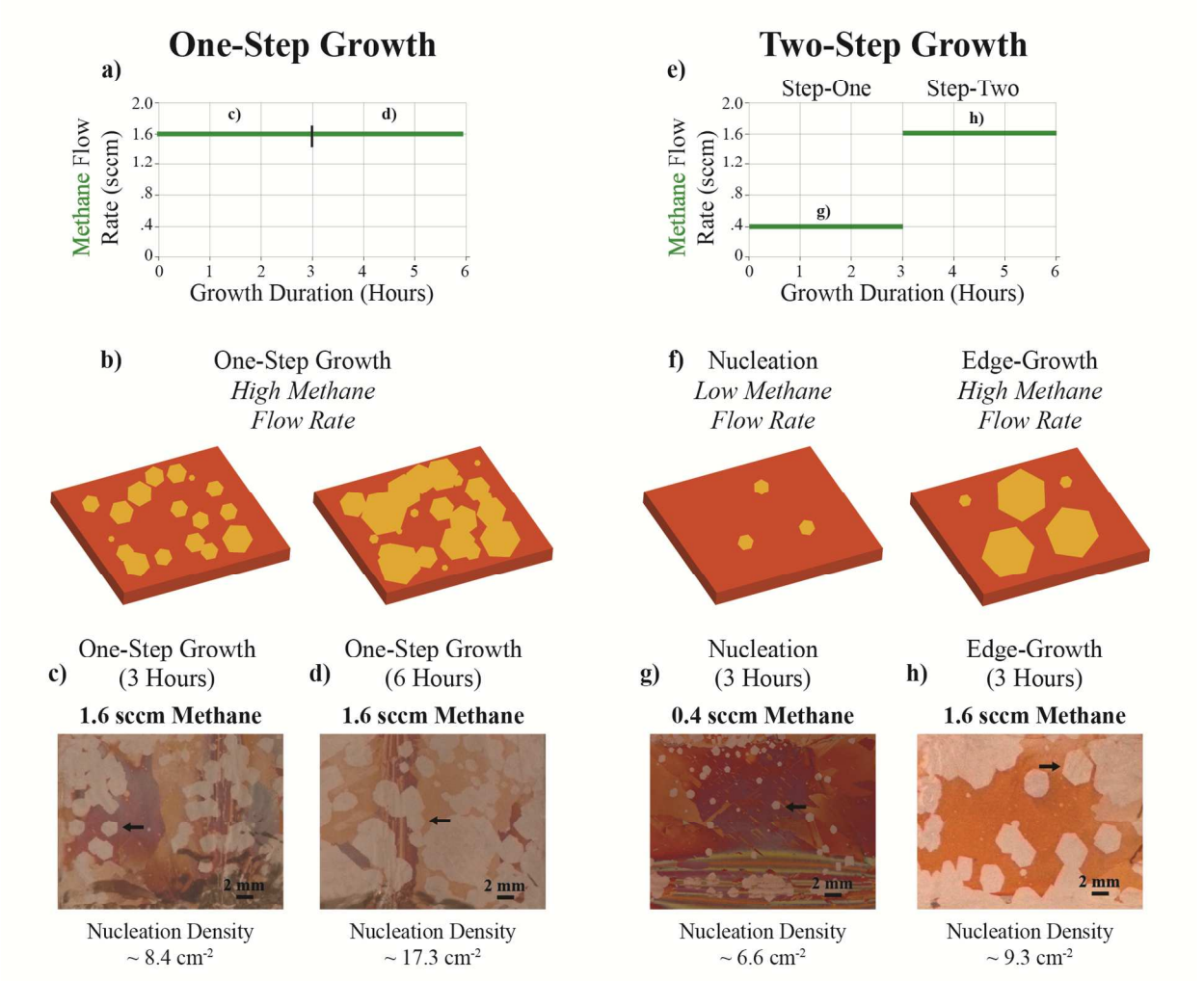

Figure 1. a) Outline of typical one-step growth, using high methane flow rate b) cartoon depicting graphene growth using high methane flow rate resulting in high nucleation density, which forms full films after long duration. c-d) Optical images of oxidized copper after one-step growth for 3-hour, and 6-hour duration. e) Outline of two-step growth, using low methane flow rate stage, followed by high methane flow rate stage. f) Cartoon depicting graphene growth using two-step growth. Step-one creates a low nucleation density by using low methane flow rates. Step-two promotes edge-growth using elevated methane flow rates. g-h) Optical images of

oxidized copper after step-one, and step-two. Step-one (.4 sccm) produces domains of low nucleation density; step-two (1.6 sccm) increases the size of isolated domains. Black arrows point to graphene domains.

The two-step growth protocol employed here, outlined in **(Fig. 1e)**, consists of a low methane flow rate stage, followed by a high methane flow rate stage. Argon and hydrogen flow rates are kept constant throughout the entire growth duration. Step-one is intended to achieving a low nucleation density in order to allow the adequate surface area to grow isolated, large-area single-domain graphene, whereas step-two is aimed at enlarging the size of existing nucleated domains (**Fig. 1f**). Previous studies using two-step growth were designed to increase the nucleation density after large-domain graphene was synthesized in order to fill-in voids, and ultimately, create large-domain films[3], whereas our main aim is to avoid merging of domains by maintaining a low nucleation density. **(Fig. 1g-h)** shows growths after step-one, and step-two, and demonstrates that despite the increased growth rate (from the increased methane flow rate) during step-two, the nucleation density is does not dramatically increase **(Fig. S5g)**, such that isolated domains are still apparent. The mechanisms that enable these experimental results are believed to be related to the diffusion of carbon species in copper, specifically to copper pocket growths, and will be discussed in detail below. Regardless of the mechanism, by using our two-step growth process, we are able to synthesize isolated, 5-mm single-domain graphene in less than 5 hours.

Following two-step synthesis, we employed a series of characterization techniques to assess the quality of the synthesized graphene, and to fully confirm that the graphene is neither polycrystalline nor multilayer. First, scanning electron microscopy (SEM) was used to image graphene on the copper foils; we found that the 120-degree angle of the domain growth front,

and the lack of observable defects or boundaries highly advocate that the synthesized graphene is single-domain[7] as shown in **(Fig. 2a)**. Optical images of transferred[17,18] single-domains onto silicon oxide (SiO_2) show that the majority of the domain area is monolayer, with only a small nucleation center consisting of ad-layer graphene present **(Fig. 2b)**. To further substantiate the growth of monolayer, single-domain graphene, we used selected area electron diffraction (SAED) to investigate the crystal structure of domains transferred[17,18] onto Transmission Electron Microscopy (TEM) grids. **(Fig. 2c)** shows a typical SAED pattern, recorded from one single domain and verifies that the graphene domain is single crystal[19]. **(Fig. S6)** shows a collection of SAED patterns from one single-domain spanning 2 mm^2. The alignment angle of the electron diffraction patterns are within 2 degrees of variation (the single domain graphene was laid on a copper TEM grid, and as a consequence, patterns recorded across large distances vary from bending of the TEM grid) and further supports the growth of single-domains[5,7]. Raman spectroscopy was used to assess the quality of single-domain graphene transferred onto an OctadecylTriChloroSilane (ODTS) modified SiO_2 substrate (as to minimize substrate effects)[20]. **(Fig. 2d)** shows a representative Raman spectra of a single-domain. **(Fig. 2e-g)** shows the intensity of the G-peak (~1583), 2D-peak(~2683), and the D-peak (~1350) collected for a sample using Raman mapping, respectively[21]. In all 3 intensity-mapping images, a clear boundary between the graphene and the substrate is obvious. A small patch of PMMA contamination near the bottom of the graphene sample is also evident[22]. The lack of D-peak[23] (except around the graphene boundary, and PMMA contamination), in addition to the large ratio of 2D:G intensities[22,24] (> 3:1) **(Fig. 2h)**, indicates a very high quality monolayer of graphene. Altogether, our characterization methods confirm that the synthesized graphene using two-step growth is monolayer, and single-domain.

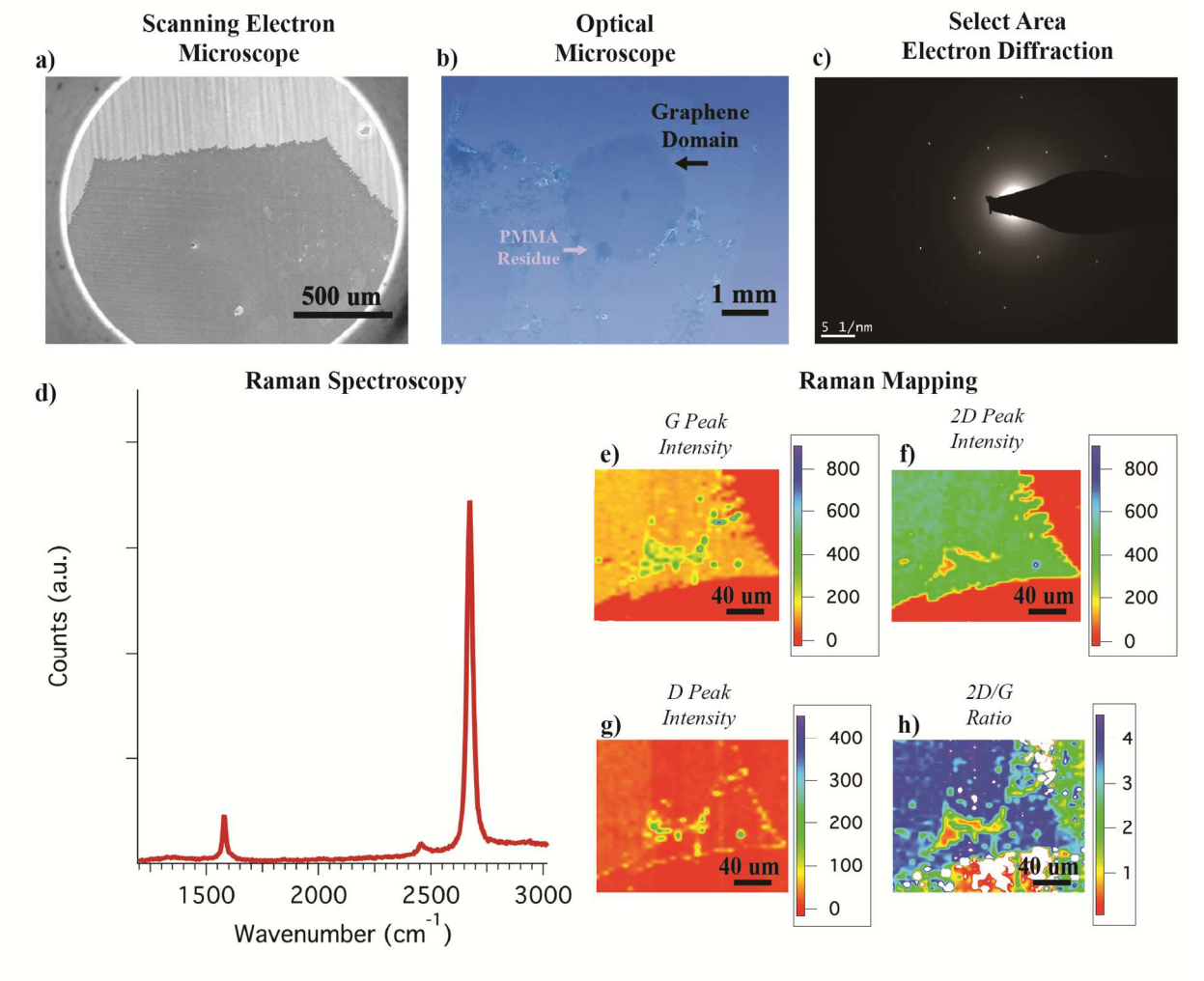

Figure 2: a) SEM image of hexagonal growth edge of large-domain graphene synthesized using two-step growth. b) Optical image of large-domain graphene transferred onto SiO_2 substrate. The majority of the domain is monolayer, with a small observable nucleation center consisting of adlayer graphene. c) A representative SAED pattern of one single-domain showing the single crystal nature of the domain. d) A representative Raman Spectra of monolayer graphene e-g) Raman mapping images of single-domain graphene on a domain corner to spatially track intensities of the G peak, 2D Peak and D Peak, respectively. Defects are observed on a small patch of PMMA contamination near the bottom edge of the domain, and on the domain-edge. h)

The ratio of the intensity of the 2D:G peaks is greater than 3:1 for the majority of the single-domain, and further confirms high quality, monolayer graphene is synthesized.

To investigate the dependence on the methane flow rate during two-step growth, we performed a series of growths, varying the methane flow rate using the two-step process. Step-one, and step-two were both held for 3-hour duration each. **(Fig. 3a)** shows an optical image of the inside surface of the copper pockets after 3 hours of low methane exposure (step-one growth). Distinct mm-sized domains appear spread across the inside surface, with the adequate spacing necessary for edge-growth during step-two (Fig S5a).

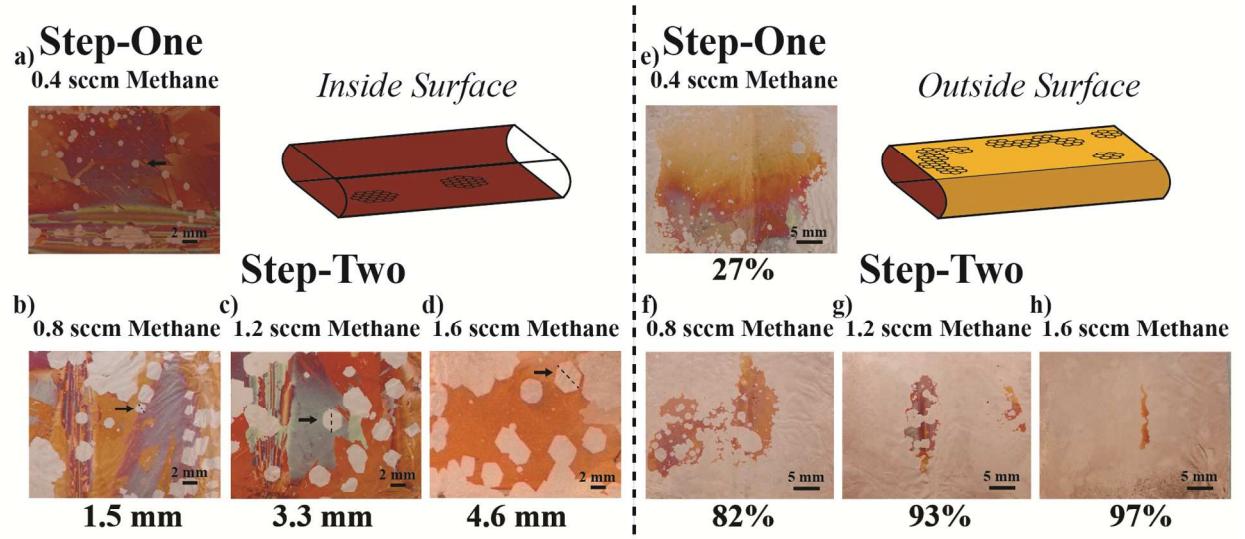

Figure 3: a) Optical image of graphene on the inside of copper pockets following copper oxidation after step-one. Step-one uses low methane flow (.4 sccm) over 3 hours to create low density of nucleation. b-d) Optical images of graphene on the inside of copper pockets following copper oxidation after two-step growth varying the second-step flow rate from .8, 1.2, to 1.6 sccm, respectively. By increasing the methane flow rate (for step-two) the average domain-size increases, without the need to increase growth duration. e-h) Optical images of graphene on the outside of copper pockets following copper oxidation after step-one and step-two. Increases in

methane flow rate (step-two) causes an increase of growth on the outside, with greater percent coverage for greater methane flow rate. Using 1.6 sccm methane for the step-two flow rate (for 3 hours) results in nearly full coverage of the outside surface. Black arrows point to graphene domains.

After defining the low nucleation density set in step-one, we monitored the effects of increasing the flow rate for step-two. **(Fig. 3b-d)** shows a series of optical images of the inside of the copper pockets after two-step growth using identical conditions for the step-one (.4 sccm), but with increasing methane flow rate for the second step, ranging from .8 – 1.6 sccm, respectively. Interestingly, by using a two-step growth process, we do not observe a dramatic increase in the nucleation density of graphene domains to the extent that isolated domains exist, even though the methane flow rate is increased incrementally for each experiment **(Fig. S5e-g)**. Moreover, as the second-step flow rate is increased, from .8 to 1.2, and then to 1.6 sccm, the average domain-size increases for respective increases in flow rate, without the need to increase the growth duration.

Using a two-step growth, it is possible to control the size of large-area single-domains by choosing the corresponding step-two methane flow rate. Compared to the single-step growth using low methane flow (.4 sccm) **(Fig. S4b)**, using a two-step growth over the equivalent growth duration, results in larger domain-sizes (for all flow rates, .8, 1.2, and 1.6 sccm). Furthermore, the increase in methane flow rate effectively increases the graphene domain-size, without the expense of additional ad-layer coverage **(Fig. S7)**. Thus, we have shown that by using a two-step growth protocol, it is feasible to promote domain-edge growth while simultaneously controlling the nucleation density.

DISCUSSION

Why does the nucleation density not increase with an increase in the step-two methane flow rate as revealed in our experiments? The use of high methane flow rate to grow large-domain graphene while retaining a low nucleation density seems contradictory to previous experiments[2,3,7–12,16], and indicates that other factors play a key role in limiting the overall nucleation density inside the copper pocket. To investigate why elevated methane flow rates could result in low nucleation density instead of full graphene films, we monitored graphene growth both on the inside and outside surface of the copper pocket following two-step growth. We observe that after step-one **(Fig. 3e)**, the majority of the outside surface remains uncovered (27% surface coverage); as the flow rate is increased from 0.8 sccm, up to 1.6 sccm for step-two, we notice that the surface coverage of the copper foil subsequently increases, up to nearly full coverage (97%) for the largest flow rate **(Fig. 3f-h)**. Clearly, increases in step-two methane flow rate increase the overall growth rate[2,13,15], generating the increase in domain-size on the inside surface, and increasing coverage on the outside surface.

We found a significant transition occurs whenever the outside surface was fully covered. When we used step-two flow rates larger than 1.6 sccm (97% outside surface coverage), such as 2.4 sccm, the inside surface contains merged graphene domains, not isolated single-domains **(Fig. 4a-b)**. This apparent increase in nucleation density corresponds to full graphene coverage on the outside surface (100%). These results provide an important clue on how two-step growth preserves a low nucleation density inside the copper pocket during elevated methane flow rates. To assess if the formation of a full film on the outside surface is related to the increase of the nucleation density inside, or merely a result of using elevated methane flow rates, we investigated the influence of the growth duration of step-two, maintaining elevated methane flow rates.

The increased growth rate that occurs from using elevated methane flow rates results in faster coverage of the outside surface; thus, by decreasing the overall growth duration we are able to probe the influence of elevated methane flow on the nucleation density on the inside surface, before a full film exists on the outside. Despite using high methane flow rates (2.4 sccm), reducing the growth duration of step-two (from 3 hours to 1.5 hours) to avoid formation of a full film on the outside, results in the growth of isolated, large-domain graphene on the inside surface **(Fig. 4c-d)**. Similar results tuning the growth duration to avoid full film coverage are shown in **(Fig. S8a-d)** for an additional elevated methane flow rate. Thus, we show that the nucleation density inside remains low, only when the outside surface remains uncovered (by adjusting methane flow rate, or growth duration). We have verified this method of synthesizing isolated large domains with over 80 successful growth runs. Regardless of the mechanisms dictating this trend, we can exploit the fast growth rate (using high methane flow rates) and curb the increase of nucleation density by avoiding full film coverage on the outside surface, in parallel. This allows the overall growth duration to be severely reduced when synthesizing isolated large-domain graphene. **(Fig. 4e)** shows an optical image of the inside of a copper foil following a two-step growth with only a 4.5-hour (total) growth duration. We are able to grow isolated, large-domain graphene up to 5 mm in domain-size utilizing the high methane flow rate of step-two, and by tuning the growth duration to avoid full films on the outside to keep nucleation low inside. The majority of the growth duration is the slow, step-one stage (3 hours), where low nucleation density is first established. Compared to other methods that utilize only a single-step growth on oxidized copper substrates, our two-step growth method can be up to 10 times faster than conventional, one-step methods[8–12] **(Fig. 4f)**. Until the ultimate goal of a wafer-scale single-domain graphene without grain boundaries is achieved, for various large-area graphene

applications where grain boundaries could be detrimental, continuous monolayer films of merged large-domains can be useful. Using our two-step method, it is simple to grow a full film (as shown in Fig. 4a) consisting of large-domain graphene on the inside surface of the copper pocket by extending the growth duration. The growth of continuous large-domain films and characterization of the large-domain grain boundaries (mm-scale) is documented in **(Fig. S9).** Altogether, by simultaneously controlling nucleation density and edge-growth, the synthesized graphene demonstrated here highlights the versatility, in terms of domain-size, growth duration, and continuous surface coverage, of the developed growth protocol.

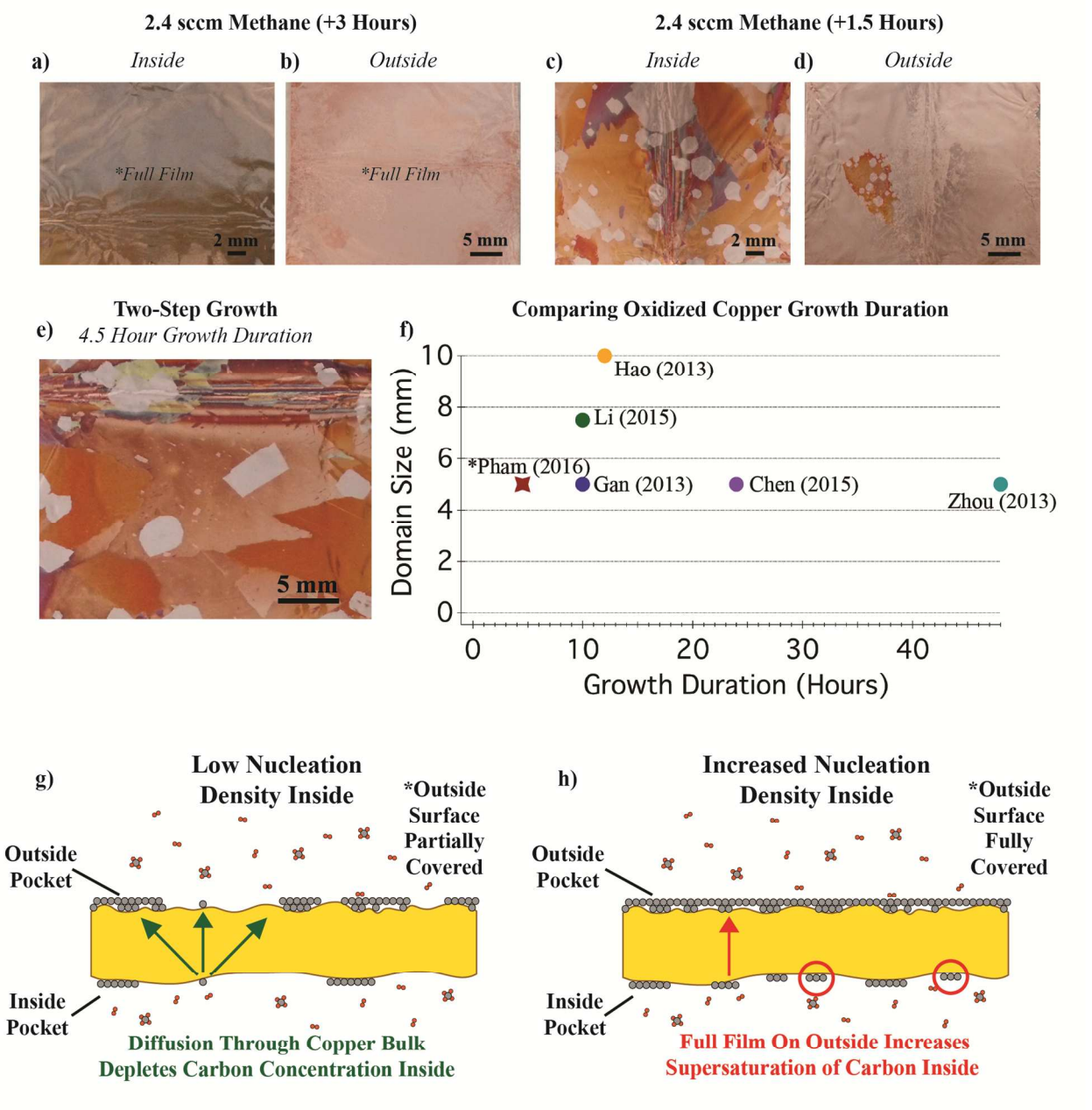

Figure 4: a-b) Optical images of inside and outside of copper pockets following copper oxidation after two-step growth. After full films cover the outside surface, growth inside produces merged domains/films. c-d) Full film coverage on the outside surface is avoided by reducing the growth time to 1.5 hours for step-two using 2.4 sccm. We observe preservation of low nucleation density inside after decreasing growth duration. e) Optical image of inside of copper pockets following copper oxidation after optimized two-step growth resulting in isolated

5-mm graphene domains. f) Comparing other oxidized copper growth durations (one-step) compared to our two-step growth. g-h) Cartoon depicting the influence on the diffusion of carbon and the inside nucleation density, before and after the formation of full films on the outside surface. After formation of a full film on the outside surface, the nucleation density inside, increases.

In order to postulate how the formation of a full film on the outside surface influences the nucleation density on the inside surface, we must consider the conditions whence nucleation occurs. Verified both by observations in our two-step studies, and in the literature, growth inside enclosed copper pockets has the characteristic trend of low nucleation density inside, resulting in larger domains on the inside surface than the outside surface[2,6,8,10]. Nucleation, in addition to edge-attachment, and ad-layer growth, results from the diffusion of carbon species on the copper surface[13,14,25–35]. The formation of large carbon chains and clusters responsible for graphene nucleation[32–35] occurs when the concentration of carbon species on the surface, $C_{Surface}$, is much higher compared to the equilibrium concentration ($C_{Nucleation} \approx 2C_{Equilibrum}$)[13,28]. On the other hand, if the level of carbon species is between the nucleation and equilibrium concentrations ($C_{Nucleation} > C_{Surface} > C_{Equilibrum}$), edge-growth of graphene can occur[13,28,30–34].

Our results suggest that, during step-one where we use a low methane flow rate, the concentration of carbon species on both surfaces remains close to the equilibrium concentration ($C_{Surface} \geq C_{Equilibrum}$), thus, in order to cause supersaturated nucleation, long growth durations (3 hours) are required. As soon as nucleation occurs, the amount of supersaturated carbon species quickly depletes[13]; hence, the low nucleation density on the inside surface[13,28]. This assumption is further supported by the nearly bare, outside surface. During step-two, when the methane flow rate is increased, we observe a dramatic increase of domain-size on the inside surface, with

negligible increase in nucleation density. This suggests that the carbon concentration on the inside surface still remains in the sensitive region between equilibrium and nucleation, ($C_{Nucleation} > C_{Inside} > C_{Equilibrum}$)[13,28]. The increasing coverage on the outside surface (for increasing methane flow rate) also agrees with a rise in the carbon concentration. It is observed that new nucleation sites on the inside surface do arise, but overall, since we are able to yield isolated domains, nucleation does not dominate, and indicates that the carbon concentration level remains close to, or below the nucleation threshold. Finally, after a full film is grown on the outside surface, indicating that the carbon concentration has remained above the equilibrium level over long durations[13], we observe increased growth on the inside surface, which results in the formation of merged domains.

From our experiments adjusting growth duration to compensate for the elevated methane flow rates, we observed that full film coverage on the outside surface acts as a convenient, observable threshold where nucleation inside remains low, such that isolated domains are synthesized. This suggests that, on the inside surface, before the formation of a full film, the concentration of carbon species is still relatively close to the nucleation threshold, ($C_{Surface} \leq C_{Nucleation}$); subsequently, after the formation of a full graphene film on the outside, we observe an increase in nucleation density on the inside, suggesting the carbon concentration on the inside increases, up to the nucleation threshold[13,28]. The tuning of growth duration would hence not be effective in limiting nucleation on the inside if the concentration of carbon species were well above the nucleation threshold before the formation of a full film on the outside, as would be in the case of extremely high methane flow rates. This regime is where previous two-step studies have typically operated[3], and we confirm these results in **(Fig. S8e-h)**. Nonetheless, for our control experiments avoiding formation of full film coverage on the outside surface to limit the

nucleation density inside, before formation of a full film on the outside surface, we believe that the carbon concentration inside is still within the sensitive range between growth and nucleation. Thus, it is plausible that the formation of a full film on the outside, could affect the concentration of surface carbon species on the inside to a large enough degree, such that, distinct changes in the nucleation rate occur. We speculate that the ability to operate in such a sensitive carbon concentration range is only enabled by the unique effects of oxidized copper growth, which are utilized during the two-step synthesis.

Although the growth pathways for CVD graphene synthesis have been widely studied both experimentally and theoretically[3,7,13,25–36], the exact evolution of graphene growth is still not fully developed, especially for oxidized copper growths[8,9,12,14]. Recently, it has been revealed that the presence of surface oxygen species not only limits the nucleation density[8,9,12], but also plays a crucial role in decreasing the edge-attachment barrier for domain growth[8], and imperative to our studies using copper pockets, enables the diffusion of carbon monomers through the copper bulk[14]. While the control of the nucleation density via passivation of active nucleation sites has been exploited in other studies growing large-domain graphene[8–12], the use of elevated methane flow rates in our studies directly utilizes the decreased edge-attachment barrier for domain growth. When using elevated methane flow rates for two-step growth, due to the decreased edge-attachment barrier, we expect that the surface carbon species can easily be incorporated into existing domains to contribute to edge growth[8]. This is supported by the fact that we see an increase in domain-size for increased methane flow rate. We observe this oxygen assisted edge-growth, despite the presence of hydrogen gas flow, which can act as a growth inhibitor[30,31]. Furthermore, with an increase in methane flow rate, we observe a variety of isolated, domain morphologies, instead of compact hexagons, which further supports utilization of an oxygen

aided, decreased edge-attachment barrier and diffusion limited growth[8], and suggest the observed domain morphologies are not directly dictated by substrate aligned growth[35,36]. This aspect of our method is dually advantageous, since carbon species that are incorporated into existing domains can quickly deplete the overall concentration of surface carbon species, preventing further nucleation[8,13,28,31]. In addition, metal step-edges, which often act as sites for nucleation, do not effectively trap carbon monomers[33]; therefore, the complete dehydrogenation of CH_4 to carbon monomers from oxygen species[8] could play a role in decreasing the nucleation density. For these reasons, a two-step growth on oxidized copper is ideal for limiting the nucleation density, since existing domains from step-one can easily incorporate and deplete the surface carbon species during step-two, resulting in a lower nucleation density compared to a one-step growth of equivalent methane flow rate and growth duration (Fig. S5e-f).

Due to the fact that our two-step method utilizes oxidized copper growth, which results in the full dehydrogenation of methane to readily yield carbon monomers, diffusion of carbon through the copper bulk is expected to occur[14,31]; this could be the underlying mechanism controlling increases in the nucleation density on the inside, after a full film covers the outside surface. Even before full film coverage, we observe areas of adlayer graphene growth on the outside surface of the copper pocket for all methane flow rates **(Fig. S10)**. Since adlayer growth on the outside surface results from the diffusion of carbon monomers originating from the inside surface[14,29], our observations suggest that during the two-step process, diffusion through the copper bulk occurs without the need for full film coverage. These results are markedly different compared to previous experiments where the formation of adlayer graphene only takes place after a full film forms on the outside surface[14,29]. Although the diffusion of carbon through the copper bulk before full film conditions (on the outside surface) has not been established, the evidence

suggests that the diffusion rates could depend on a number of factors on both surfaces, including the nucleation density, exposed copper surface areas, adlayer nucleation density, and concentration of surface oxides[14,29–31], but the optimization of these parameters is beyond the scope of this paper. However, our observations of distinct variations (in domain size and coverage) in adlayer growth on the outside surface (Fig S10) indicate that the diffusion of carbon, feeding adlayer growth on the outside can be altered upon changes in the methane flow rate; thus it is reasonable to speculate that the real time diffusion of carbon species through the copper bulk can influence the local carbon concentration on the inside surface during growth.

One possible explanation of why the nucleation density remains low on the inside surface before full film conditions during two-step growth is that the diffusion of carbon through the copper bulk can "store" excess carbon as adlayer growth where metal defects or impurities exists[31,33]. Increases in the carbon concentration on the inside surface during two-step growth could thus drive the diffusion rate through the copper bulk[14]. This allows the local carbon concentration on the inside to remain below the nucleation threshold as carbon species are depleted from the inside surface **(Fig. 4g)**. After the formation of a full film, we observe an increase in the nucleation density on the inside surface (implying an increase of the local carbon concentration) **(Fig 4h)**. We have not confirmed where the increase of the carbon concentration arises from, but consider that a decrease of carbon diffusion through the copper bulk could result as a consequence of a decreased concentration gradient as adlayer coverage increases on the outside surface[14]. This hypothesis that the diffusion rate through the bulk is determined by full film conditions (such as nucleation density, copper surface coverage) is consistent with previous studies demonstrating a correlation of the inside nucleation density to adlayer coverage on the outside surface[29]. Further investigation on the diffusion mechanism during two-step growth

could foster development of new methods to severely suppress nucleation on the inside surface, and improve bilayer synthesis on the outside surface.

The methods and techniques developed here, simultaneously controlling nucleation density and edge growth, should be adapted to other graphene growth substrates to further extend current single-domain size limits and rates. The fast two-step growth protocol for growing large single-domain graphene can be easily modified to other metallic growth substrates, where graphene nucleation and edge growth can be separated into two steps, including but not limited to platinum, ruthenium, iridium, and palladium[37–39]. The increased catalytic activity for CH_4 and H_2 dissociation on platinum for example[37], could provide additional means for accelerating the growth rates of graphene single-domains when used in combination with a two-step protocol. Additionally, the two-step growth method could realize the synthesis of large-domain graphene from the seamless stitching of aligned graphene nucleation centers[35].

Methods to limit the nucleation density and growth rate by controlling the carbon diffusion through the bulk, as investigated in this work, could be further examined using metals such as nickel[40], where the increased carbon solubility, and carbon segregation growth mechanism could provide an obvious means to regulating the local carbon concentration, and hence, large-domain graphene growth. Methods using nickel and ruthenium substrates under controlled carbon segregation conditions have already demonstrated utility for growing mm-scale monolayer domains[41,42]; combined with the techniques developed here on copper, it is reasonable to anticipate metals such as these (as alloys, layered stacks, or pure metals) as appropriate growth substrates for synthesis of wafer-scale single-domain monolayer graphene or large-domain bernal stacked graphene.

CONCLUSION

We have demonstrated a simple method for fast synthesis of mm-domain-size graphene using a two-step oxidized copper growth inside copper pockets. The two-step approach, which is supported from oxidative-assisted mechanisms to control nucleation, promote edge growth, and drive carbon diffusion through the copper bulk, exploits the low nucleation density using low methane flow rates, which are then enlarged using increased methane flow rates. We find that the outside surface of the copper pocket acts as an observable threshold where the nucleation density remains low inside. Thus, we can easily tune the first and second stage durations and methane flow rates according to the coverage on the outside copper surface to obtain isolated, large-domain graphene. Applying this method, we show that 5-mm single-domains can be synthesized in 4.5 hours of growth. A host of characterization techniques were employed to confirm that the synthesized graphene is monolayer and single-domain. Our studies focused on optimizing growth conditions can be adapted to most existing CVD systems, and will promote the development of synthesizing wafer-scale single-domain graphene, which will further stimulate advances in graphene integration and applications.

Supporting Information.

Supporting Information Available: Methods, pre-growth optimization, additional characterization, and nucleation density assessment and controls. This material is available free of charge via the Internet at http://pubs.acs.org.

Corresponding Author

Address Correspondence to pburke@uci.edu

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflict of Interest

The authors declare no competing financial interests

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