

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

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Supporting Information

ABSTRACT: We report a two-step chemical vapor deposition 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 h 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 coverage¹⁻³ prior to the growth of large domains. This results in multiple detrimental grain boundaries⁴ due to the polycrystalline nature of multidomain films.⁵ The ultimate goal, and the 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 times⁸⁻¹² 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 pocket⁶ 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 dehydrogenation 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 bulk¹⁴ in both directions). This "window" has not been explored previously in the literature. Furthermore, we show that this window of opportunity exists

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Figure 1. (a) Outline of typical one-step growth using a high methane flow rate. (b) Cartoon depicting graphene growth using a high methane flow rate, resulting in high nucleation density, which forms full films after a long duration. (c and d) Optical images of oxidized copper after one-step growth for 3 and 6 h durations. (e) Outline of two-step growth using a low methane flow rate stage followed by a high methane flow rate stage. (f) Cartoon depicting graphene growth using two-step growth. Step one creates a low nucleation density using low methane flow rates. Step two promotes edge growth using elevated methane flow rates. (g and h) Optical images of oxidized copper after steps one and two. Step one (0.4 sccm) produces domains of low nucleation density; step two (1.6 sccm) increases the size of isolated domains. Black arrows point to graphene domains.

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 h of total growth time, much faster than traditional onestep 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 (Figure S1). Before growth optimization (two-step growth) experiments were conducted, we monitored and adjusted pregrowth 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 Figure S2. These parameters are held constant throughout the remainder of experiments, including two-step growth studies (Figure S3).

Typically, for one-step growth procedures, a low methane flow rate is used over long durations 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 especially since the growth rate decreases overtime.¹⁵ As verified in (Figures S4a and b), when using a low methane flow rate (0.4 sccm), distinct millimeter-sized domains appear in low densities (Figures S5a and b), but long growth durations have limited effects on increasing domain size. To assess if a high methane flow rate could be used to synthesize 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 over time (Figure 1a). Following growth, the enclosed copper pockets are cut open and oxidized on a hot plate to reveal graphene growth coverage.¹⁶ Figures 1b-d show 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 (Figures S5c and 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, to synthesize large-domain graphene using an increased methane flow rate (to decrease the overall growth duration) without the detriment of increased nucleation density



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 a SiO₂ 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, 2D, and D peaks, 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 that high quality, monolayer graphene is synthesized.

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

The two-step growth protocol employed here and outlined in Figure 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 achieve a low nucleation density 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 (Figure 1f). Previous studies using two-step growth were designed to increase the nucleation density after large-domain graphene was synthesized 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. Figures 1g and h show growth after steps one and two and demonstrate that, despite the increased growth rate from the increased methane flow rate during step two, the nucleation density does not dramatically increase (Figure 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 are 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 h.

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° 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 Figure 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 adlayer graphene present (Figure 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. Figure 2c shows a typical SAED pattern recorded from one single domain and verifies that the graphene domain is single-crystal.¹⁹ Figure S6 shows a collection of SAED patterns from one single domain spanning 2 mm². The alignment angle of the electron diffraction patterns are within 2° of variation (the single domain graphene was laid on a copper TEM grid, and as a consequence, patterns recorded across large distances vary



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 (0.4 sccm) over 3 h 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 0.8, 1.2, to 1.6 sccm, respectively. When the methane flow rate (for step two) is increased, 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 steps one and two. Increases in methane flow rate (step two) causes an increase in growth on the outside with a greater percent coverage for greater methane flow rate. Using 1.6 sccm methane for the step two flow rate (for 3 h) results in nearly full coverage of the outside surface. Black arrows point to graphene domains.

from bending of the TEM grid), which 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 SiO₂ substrate to minimize substrate effects.²⁰ Figure 2d shows a representative Raman spectra of a single domain. Figures 2e-g show the intensity of the G-peak (~1583), 2D-peak(~2683), and the Dpeak (~1350) collected for a sample using Raman mapping.²¹ In all three 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-peak²³ (except around the graphene boundary, and PMMA contamination), in addition to the large ratio of 2D:G intensities^{22,24} (>3:1) (Figure 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 singledomain.

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. Steps one and two were both held for 3 h durations each. Figure 3a shows an optical image of the inside surface of the copper pockets after 3 h of low methane exposure (step one growth). Distinct millimeter-sized domains appear spread across the inside surface with adequate spacing necessary for edge growth during step two (Figure S5a).

After defining the low nucleation density set in step one, we monitored the effects of increasing the flow rate for step two. Figures 3b–d show a series of optical images of the inside of the copper pockets after two-step growth using conditions identical to those of step one (0.4 sccm) but with increasing methane flow rate for the second step ranging from 0.8–1.6 sccm. Interestingly, by using a two-step growth process, we did 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 (Figures S5e–g). Moreover, as the second-step flow rate is increased from 0.8 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 twostep methane flow rate. Compared to the single-step growth using low methane flow (0.4 sccm) (Figure S4b), using a twostep growth over the equivalent growth duration results in larger domain sizes (for all flow rates, 0.8, 1.2, and 1.6 sccm). Furthermore, the increase in methane flow rate effectively increases the graphene domain size without the expense of additional adlayer coverage (Figure 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 (Figure 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 (Figures 3f-h). Clearly, increases in step two methane flow rate increase the overall growth rate,² generating the increase in domain size on the inside surface and increasing coverage on the outside surface.

We found that a significant transition occured 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



Figure 4. (a and b) Optical images of the 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 and d) Full film coverage on the outside surface is avoided by reducing the growth time to 1.5 h for step two, using 2.4 sccm. We observe preservation of low nucleation density inside after decreasing growth duration. (e) Optical image of the inside of copper pockets following copper oxidation after optimized two-step growth, resulting in isolated 5 mm graphene domains. (f) Comparison other oxidized copper growth durations (one-step) to our two-step growth. (g and 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.

domains, not isolated single-domains (Figures 4a and 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 in 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 to 1.5 h) to avoid formation of a full film on the outside surface (Figures 4c and d). Similar results tuning the growth duration to avoid full film coverage are shown in Figures 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 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. Figure 4e shows an optical image of the inside of a copper foil following a twostep growth with only a 4.5 h (total) growth duration. We were 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 and to keep nucleation low inside. The majority of the growth duration is the slow, step one stage (3 h), 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 $^{8-12}$ (Figure 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 Figure 4a) consisting of largedomain 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 (millimeter scale) is documented in Figure S9. Altogether, by simultaneously controlling nucleation density and edge growth, the synthesized graphene demonstrated here highlights the versatility of the developed growth protocol in terms of domain size, growth duration, and continuous surface coverage.

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 by the literature, growth inside enclosed copper pockets has the characteristic trend of low nucleation density inside, resulting in domains on the inside surface larger than those on the outside surface.^{2,6,8,10} Nucleation, in addition to edge attachment and adlayer 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 ($C_{\text{Nucleation}} \approx 2C_{\text{Equilibrum}}$).^{13,28} On the other hand, if the level of carbon species is between the nucleation and equilibrium concentrations ($C_{\text{Nucleation}} \lesssim C_{\text{Surface}} > C_{\text{Equilibrum}}$), 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, to cause supersaturated nucleation, long growth durations (3 h) 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 in domain size on the inside surface with a 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 ($C_{\text{Nucleation}} > C_{\text{Inside}} > C_{\text{Equilibrum}}$).^{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, because we are able to yield isolated domains, nucleation does not dominate, and this 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 and 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 Figures S8e-h. Nonetheless, for our control experiments that avoid formation of full film coverage on the outside surface to limit the nucleation density inside and 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 enabled only 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 edgeattachment 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 control of the nucleation density via passivation of active nucleation sites has been exploited in other studies growing large-domain graphene, $^{8-12}$ 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 growth⁸ and suggests that the observed domain morphologies are not directly dictated by substrate aligned growth.^{35,36} This aspect of our method is dually advantageous because 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 species⁸ 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 because 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 onestep growth of equivalent methane flow rate and growth duration (Figures S5e and 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 (Figure S10). Because 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 those of previous experiments where the formation of adlayer graphene takes place only 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 (Figure 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 (Figure 4g). After the formation of a full film, we observe an increase in the nucleation density on the inside surface, implying an increase in the local carbon concentration (Figure 4h). We have not confirmed from where the increase in the carbon concentration arises, but we consider that a decrease in 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 or 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 twostep 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 that simultaneously control 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 twostep 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 millimeter-scale monolayer domains.^{41,42} When combined with the techniques developed here using copper, it is reasonable to anticipate metals such as these (as alloys, layered stacks, or pure metals) are appropriate growth substrates for synthesis of wafer-scale single-domain monolayer graphene or large-domain bernal stacked graphene.

CONCLUSION

We demonstrated a simple method for fast synthesis of millimeter-sized domain graphene using two-step oxidized copper growth inside copper pockets. The two-step approach, which is supported from oxidative-assisted mechanisms to control nucleation, promotes edge growth, drives carbon diffusion through the copper bulk, and 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 h 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 that 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.

ASSOCIATED CONTENT

Supporting Information

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Methods, pregrowth optimization, additional characterization, and nucleation density assessment and controls (PDF)

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Notes

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Supporting Information

METHODS

Preparation of Copper Foil for CVD Growth

To prepare copper foils for CVD growth, one side of a $\sim 5 \text{ x} 5 \text{ cm}$ sample of 25um thick copper foil from Alfa Aaser (#13382) is electropolished for 1 minute at 5 V in a solution of deionized water, phosphoric acid, ethanol, isopropyl alcohol, and urea as described in Ref[1]Following rinsing in deionized water and ethanol, the copper sample is gently blown dry, and placed on a 200 C hotplate for 1 min to undergo surface oxidation. Due to the findings in (Fig. S2), samples are typically oxidized for 1 minute, as this was found to be the optimal heating duration. The copper foil is then folded in half, and the sides are carefully crimped to create a copper pocket for CVD growth as seen in (Fig. S1).



Figure S1: Optical images of construction of enclosed copper pockets following electropolishing and hotplate oxidation of \sim 5 x 5 cm copper foil. Copper foil is folded in half, and the remaining 3 sides are carefully crimped to create the enclosed copper pocket. Dotted line shows where the copper foil is folded/crimped.

CVD Growth of Graphene

CVD growth of graphene is performed using a First Nano Easy Tube 3000 inside a 5inch quartz tube. Copper pockets are loaded into the growth chamber and the tube is evacuated at the beginning of each growth. (Fig. S3) depicts a typical growth recipe. The furnace is heated to the desired growth temperature under argon, followed by a 45 minute anneal in 33% hydrogen. We chose to expose the copper samples to an additional 50% oxygen exposure at elevated temperatures for 6 minutes to further suppress nucleation. Graphene synthesis is allowed to occur under the flow of 100 sccm argon, 150 sccm hydrogen, and .4 - 2.4 sccm methane while constantly evacuated by a dry scroll vacuum pump.



Figure S2: Using a standard low methane flow (.4 sccm) growth recipe, we test a number of pregrowth conditions to optimize growth inside copper pockets. a-c) depicts the influence of pre-oxidation of copper substrates on a hotplate. We find that with no oxidation, and long oxidation (2-hour), the nucleation density is higher than that of samples that are only oxidized for a short time (1-min). e-f) We confirm that heating the CVD furnace under argon instead of hydrogen results in much lower nucleation density, due to the preservation of the surface oxide. g-i) We also examined the influence of hydrogen annealing after reaching the desired growth temperature. We observe that for low (10%) and high (60%) hydrogen concentration results in a higher nucleation density than that of medium (33%) hydrogen concentration during annealing.



Figure S3: A general outline for typical two-step growth including pre-growth optimization.



Figure S4: a-d) The results of control experiments for one-step growth for .4 sccm and 1.6 sccm for both 3 hours and 6 hour growth duration. Black arrows are provided to identify single-domains. Low methane flow rates produce distinct, individual domains that are limited in size, while elevated flow rates yield larger, merged domains.

Assessing Nucleation Density

The inside surface is observed to have varying local (across centimeters) nucleation densities (possibly from defects and impurities). Isolated domains inherently require a low local nucleation density. Since our goal was to synthesize isolated domains, we estimate the nucleation density proximal to distinct isolated domains. We used a square of 1.5 cm width to ensure that the reported nucleation density surveys an area larger than one single domain. For each growth recipe, several runs were performed to confirm that a low local nucleation density was not an anomaly of one single run; the selected images are representative of our findings.



8.8 cm⁻²

9.7 cm^{-2}

9.3 cm⁻²

Figure S5: To estimate the local nucleation density for both one-step and two-step growth procedures, we used a standard of an area of 1.5 cm width to assess locations of low nucleation. a-b) shows the nucleation density for a one-step growth using low methane flow rates which results in low nucleation density. c-d) shows an increase of the nucleation density as the methane flow rate is increased for a one-step growth. e-g) shows that when using a nucleation step, allows the nucleation density to remain low, despite using elevated methane flow rates compared to one-step growth of the same flow rate and growth duration.

Transfer and Characterization of CVD Grown Single-Domains

Following graphene synthesis, copper pockets are unfolded and heated on a hotplate to help visualize graphene coverage and enhance visual contrast. Graphene, which has been synthesized on the foil, protects the underlying copper from oxidation, and thus appears beige in color compared to the orange, red, and green hue of the oxidized copper regions which graphene did not growth.

In order to transfer graphene domains, a traditional wet transfer process is employed, using poly(methyl methacrylate) (PMMA) as a polymer support. The backside (outside of the copper pocket) is cleaned in oxygen plasma to reduce contamination during the transfer process. Copper is etched in 5% ammonium persulfate (APS) solution and cleaned in deionized water (DI). Following transfer to a self-assembled monolayer (SAM) functionalized substrate, the graphene film is dried and heated to 130 C to promote substrate adhesion. PMMA is removed in acetone and rinsed with isopropyl alcohol.

Single-domain graphene was also transferred onto TEM grids for select area electron diffraction characterization using a PMMA wet transfer method. SAED was performed in FEI/Philips CM-20 conventional TEM at 80 kV accelerating voltage.

Graphene domains are transferred onto ODTS modified substrates as to minimize substrate effects. To prepare the ODTS SAM, wafers are first cleaned in a hot piranha solution. After piranha clean, the wafers are quickly rinsed in DI water and loaded into a dry glove box in order to ensure low humidity and to preserve the hydroxyl groups necessary for SAM formation. The wafers are then placed in a solution ratio of 1:1000 ODTS:Toluene by volume for 1 hour for SAM formation.

SEM images were taken in a FEI Magellan. Raman spectroscopy measurements were performed in a Renishaw Invia Raman Spectrometer using a 532 nm wavelength excitation laser and Streamline HD mapping function.

Image J software was used to analyze surface area coverage percentage of optical images of copper foils.



Figure S6: SAED patterns of single-domain graphene over 2-mm² area. The alignment angle of the electron diffraction pattern varies by less than 2 degrees, and further supports the synthesis of large-area single-domains.



Figure S7: Optical images of large-domain graphene transferred onto SiO_2 substrate. The domain-size increases for increases of step-two, methane flow rate, without expanding the area of the adlayer nucleation center.

Control Experiments Preventing Full Film Growth

Within Nucleation Threshold



Beyond Nucleation Threshold



Figure S8: Control experiments for limiting nucleation density by monitoring outside growth coverage. a-b) Using 2.0 sccm methane for 3 hours produces increased nucleation density inside, due to full coverage of growth outside. c-d) If we reduce growth duration to 2 hours, we maintain the low nucleation density inside and observe that the copper surface on the outside is not fully covered. e-h) For very high methane flow rates (2.7 sccm, 3.0 sccm) the growth rate is pushed beyond the nucleation threshold, thus diffusion through the copper bulk is not adequate to limiting the nucleation rate when the outside surface is persevered (even when restricting growth to 1 hour), as evident in the widespread formation of small-domain graphene in between large domain sites. At 3.0 sccm (1 hour) the largedomains are almost indistinguishable from the formation of films.

Growth Of Continuous Monolayer Film

We investigated the merging of the large-domain graphene to form full films as the two-step growth duration progressed. Fig. S5a-d shows the growth of isolated largedomains from short growth periods (as demonstrated as the main goal of this paper), until the merging of these isolated domains (towards a continuous film) as the growth duration is extended. The time evolution of the two-step growth suggests that the resultant continuous films start off as large-domain graphene, and possibly concludes with some areas being patched together by smaller domains, which nucleate as the growth extends. We further investigated the merging of these films using SEM. Fig. S5e-f shows SEM images of graphene on copper on an area shortly before the full merging of large-domain crystals; an arrow is provided to help locate where two distinct large-domains merge with no observable defects. The large growth front observed under SEM before full film growth suggests the merging of large-domains consists of domains at least hundreds of microns in size. Fig. S5g-h shows a continuous 1cm x 1cm large-domain film transferred onto a SiO2 substrate. Under optical microscopy, no detrimental defects other than the typical, transfer-induced features such as wrinkles, tears, and PMMA residual contamination are observed. To further confirm that the continuous graphene film consists of large-domain graphene, we employed UV exposure of the full films after growth on copper to reveal the grain boundaries². Following 30 minutes of UV exposure in ambient conditions (~45% humidity), grain boundaries are observed by the preferential oxidization of copper beneath the boundary. Fig. S5 i-j shows optical microscopy images of a full film and an observable grain boundary following UV exposure. We observed grain boundaries on the order of millimeters in length, which further suggest that largedomains merge together to form continuous films.



Full Films After UV Exposure



Figure S9:a-d) optical images of graphene on copper foil following two-step growth ranging from 4.5 – 6.0 hours of total growth. As the growth duration proceeds, the large graphene domains start to merge and form a film. e-f) SEM images of an area before full merging g-h) optical images of continuous films transferred onto a rigid substrate i-j) optical images of graphene on copper following UV exposure to observe large-domain grain boundaries



Figure S10: SEM images of the outside of the copper pocket following two-step growth (using .4 sccm methane for step-one) for various methane flow rates. Adlayer growth is observed for all two-step growths. Our results suggest that the adlayer growth outside and the large-domain growth inside are closely related.

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