Inside the CVD “Black Box”: A Physics-Driven Exploration of Reactor Conditions during Graphene Growth

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Abstract

Though more than a decade has passed since the first report of the chemical vapor deposition (CVD) of graphene on metal substrates, the CVD reactor resembles something of a black-box. The process flow conditions, and, temperature and reactant distribution profiles are poorly understood which causes significant repeatability and reproducibility issues. This also affects studies on the growth mechanism of graphene and the synthesis of completely defect free products. To address these challenges, the open source computational fluid dynamics toolbox OpenFOAM is used for the first systematic exploration of reactor conditions for the synthesis of single crystal and single layer graphene (SLG) in a tube reactor that is typically used in the laboratory. It is found that the reactor flow conditions are in the turbulent regime, and, the temperatures of the 50-100 μm thick copper foils on which graphene is grown are not uniform but have large temperature gradients with a sensitivity to the system pressure, the total mass flow rate and the process gas composition that increases with decreasing foil thickness. Furthermore, both the foil and gas temperatures can be manipulated by modifying the mass flow rates of Ar and H₂ in the process gas mix. Finally, by combining simulation and experimental data, a process window was identified where the amount of Ar gas in the reactor was optimized to mimic cold-wall like conditions inside the hot-wall reactor and that favored the synthesis of pristine SLG films (while hotter reactor conditions produced films with numerous unwanted adlayers).

Keywords: single crystal graphene, adlayer-free, Chemical Vapor Deposition (CVD), Computational Fluid Dynamics (CFD), OpenFOAM, heat transfer
Graphene Product

‘Black Box’ CVD Reactor

CFD Simulations

Experiments

Ar, H₂, CH₄

‘excess’ Ar

‘less’ Ar

Single Layer Graphene

100 µm
Introduction

The two-dimensional (2D) material graphene, discovered by surface scientists in the 1960’s and 1970’s in studies of carbon films formed on single crystal substrates,¹⁻³ is well known for its unique properties and applications.⁴⁻⁹ Single layer graphene (SLG), is a single layer of sp²-hybridized carbon, that is a zero band-gap semiconductor with high thermal conductivity and mechanical strength. Bilayer, trilayer and few-layered graphene, respectively composed of two, three or a few graphene layers have similar interesting properties and applications. High quality defect-free graphene is generally required for applications such as in the opto-electronics industry, where the graphene film must be single-crystalline over large areas, and, without additional carbon adlayers, folds and wrinkles.¹⁰⁻¹²

Though several methods such as mechanical exfoliation¹³⁻¹⁶ of graphite and chemical processing¹⁷ of graphite oxide have been explored for graphene synthesis, chemical vapor deposition (CVD) on metal substrates remains the method of choice for synthesizing high quality and large area graphene. The CVD process offers greater control on the quality of the graphene films obtained and the CVD synthesis of graphene films that are single-crystalline over large areas have been previously reported.¹⁸,¹⁹

The CVD synthesis of graphene was first reported on nickel²⁰ films and copper²¹ foils in 2009. Since then, several CVD processes for graphene synthesis have been reported: on different metal foils or wafer supported metallic films, from different solid, liquid or gaseous precursors and using different sources of energy (thermal, plasma etc.).¹⁸ All these processes have one major disadvantage in common, it is non-trivial to near-impossible to reproduce them. For processes that can be reproduced, it may require weeks of re-optimization experiments. Moreover, repeatability issues such as an optimized growth condition changing over time in the same reactor are well known in the graphene CVD community. Such repeatability and reproducibility issues are also
common with the CVD synthesis of other 2D materials like hexagonal boron nitride (h-BN) and for carbon and other types of nanotubes. This major disadvantage significantly limits the ability of researchers to build up on results previously reported in literature and rapid progress of the field. At its worst, previously designed processes cannot be reproduced and are essentially lost.

One of the key reasons for such repeatability and reproducibility problems is that the CVD reactor, to this day, mostly remains a ‘black box’ inside which flow and temperature fields, as well as reactant concentrations are virtually unknown. Thus, though the external parameters fed into the system and the final product are known, the conditions in which chemical reactions occur and graphene grows, as well as the actual reactive species are not. Thus, attempts so far to understand the process at the molecular level and study growth kinetics have had significant gaps as the reactant side and conditions (such as, temperature of the metal foil) of the reactions being studied are uncertain. This also makes correlating theoretical simulations at the atomistic level to experimental data problematic. Finally, owing to the nano-scale dimensions of these materials, an enhanced sensitivity to controllable external parameters may be expected. All these limitations have, in turn, restricted the ability to scale-up processes and grow, for example, single crystal graphene (and other nanomaterials) on larger scales.

Given this background, in this paper, we have studied the reactor conditions for growing adlayer-free single crystal SLG films on Cu(111) foils\textsuperscript{22} and explored how different reaction environments around the foil produce different graphene films, by combining graphene growth and simulation data. While there have been previous attempts to simulate reactor conditions for the CVD growth of nanomaterials,\textsuperscript{23} to the best of our knowledge, this is the first systematic exploration for 2D materials synthesis. In the context of this work, an undesirable graphene film is one which is no longer a single-layer film but has several additional graphene islands or adlayers.
(Figure 1). These adlayers are generally up to ~20 μm in size with undefined or well-defined hexagonal shapes (i.e. bilayer or multi-layer graphene islands).

The ‘Results and Discussion’ section below is organized into two parts (Figure 2). In the first part, we have explored the flow dynamics inside our tube reactor by simulating Ar only gas flows in the reactor, with and without copper foils, when at room temperature and when heated to the graphene growth temperature, in order to understand what the conditions inside the reactor are typically like. In the second part, we have simulated and studied ‘real’ experiments that form single-crystal SLG films on Cu(111) foils and combined experimental (graphene growth) and simulation (CFD or computational fluid dynamics) data to understand the graphene growth process. Thus, we have studied what factors affect this process by exploring the reaction environment (around the foil) defined by (1) the velocity field of the process gases, (2) the thermal field of the process gases, and more importantly, of the catalytic copper foil, and, (3) the carbon precursor concentration near the copper foil, as, it is this ‘reaction environment’ that controls the graphene growth process and the final film quality. The input parameters (boundary conditions) for all simulations in this paper are based on measured data from our CVD system.

**Results and Discussion**

*Methodology Selection*

**Continuum Mechanics Model**

Figure 3 shows a schematic of the CVD system for graphene growth. This is a tube reactor equipped with a furnace, a roughing pump and mass flow controllers (MFCs). The macro-parameters that are generally known or monitored in a typical CVD experiment include the reactor pressure at the outlet, the furnace set-point, and, the mass flow rates of the process gases in standard (at 1 atmosphere and 273 K) cm³/s (sccm). SLG was synthesized at 100 torr, with a furnace set
point of 1323 K, and flows of Ar, H₂ and 0.1 mole% CH₄ in Ar (referred to as diluted CH₄ for the rest of the paper), on home-made Cu(111) foils. As shown in Table S1, Knudsen numbers for the process gases Ar, H₂ and CH₄ at room temperature (RT, 293 K) and 1323 K are much less than 0.01. Hence, continuum mechanics was used to simulate these processes. Here, the opensource CFD toolbox OpenFOAM has been used to simulate the graphene growth processes that can therefore be reproduced or extended to other CVD reactors. That OpenFOAM is opensource means that it can be modified whenever required, and as it is free to use, simulations can be much more readily reproduced by others.

If only the reactor tube were considered, typical gas velocities in the CVD reactor at 100 torr are very low, < 10 ms⁻¹, with correspondingly low Mach numbers Ma ~0.03 (the sonic velocity in Ar at 100 torr is ~321 ms⁻¹); thus, the flow may be considered to be incompressible (Table S2). However, the pipelines delivering the process gases to the reactor and the reactor inlet had a diameter of 4 mm while the reactor tube had a diameter of 46 mm. This led to a much larger Ma of 0.456 at the inlet. The gases were also heated to high temperatures, from ~293 K to ~1323 K, and this again introduced a significant variation in density, from ~0.05 – ~0.22 kgm⁻³. Thus, compressible solvers within OpenFOAM had to be used to simulate the flow conditions inside the reactor. Again, as the reactor contained both fluid and solid regions, the process gases and the copper foil, conjugate heat transfer inside the reactor was simulated by solving the energy equation for both the solid and the fluid phases in addition to the continuity and the momentum equations for the fluid phase only. Since the reactor temperatures were quite high, radiation effects were also considered.

Methane Gas Transport Hypothesis
Generally, the amount of methane in the mix was very small (Table S3), and hence, methane was considered a passive scalar that did not affect the flow fields or temperature distributions. For the same reason, no gas-phase CH$_4$-H$_2$ reactions were considered for calculating the flow properties. Thus, initial simulations were performed with only the Ar-H$_2$ mixture and at the final step, methane transport was simulated by using a scalar transport equation. Details of all OpenFOAM solvers used have been provided wherever appropriate and, in the SI (Supporting Information).

**Part 1. What are the Flow Conditions inside a Tube Reactor Typically Like?**

*Flow Dynamics in an Empty Tube Reactor at Room Temperature*

Prior to simulating the actual growth process at high temperatures, the flow inside the empty reactor at RT was first explored (condition T0, Table S3). Substituting all the gases for a typical graphene growth experiment with Ar resulted in a total mass flow rate of 229 sccm (Table S3). At 100 torr, 229 sccm of Ar flowing in the CVD tube at RT had an average velocity of 1.11 m$^{-1}$ and a $Re$ (Reynolds number) of 492 (Table S2); thus, the flow was in the laminar regime. However, the average velocity and $Re$ at RT at the much smaller reactor inlet were 146.61 m$^{-1}$ and 5654 respectively (Table S2), indicating a turbulent flow regime. Additionally, the greater than 100 times expansion in area from the inlet to the rest of the reactor tube could be expected to introduce turbulence into the system. Thus, the flow inside the reactor was considered to be turbulent and solved with a turbulence model (the $k$-$\omega$ SST model, with details provided in the SI).

For the inlet velocity $U$, the empirical power-law velocity profile of a fully developed turbulent flow was adapted,\textsuperscript{28} with $n = 6$:

$$U(r) = U_c \left(1 - \frac{r}{R}\right)^{\frac{1}{n}}$$
where, $U_c$ is the centerline or axial velocity, $r$ is the radial distance from the centerline, and, $R$ is the inlet radius. The turbulent intensity $Ti$ at the inlet was calculated based on the $Re$, as: $Ti = 0.16*Re^{-1/8}$; this was equivalent to a $Ti$ of 5.4%. The turbulent kinetic energy per unit mass or $k$ was calculated using this $Ti$ and velocity profile as $k = 1.5*(Ti*U)^2$. The specific dissipation rate $\omega$ was set to a fixed value of 63614 s$^{-1}$ based on the average velocity (please see SI for details). The reactor pressures were measured near the inlet and the outlet (Figure 3), and, the outlet pressure of 100 torr was used as a fixed value boundary condition (BC). A minimal drop in pressure across the reactor tube was observed (< 1 torr). All solver details and BCs used can be found in SI.

The gas flowed into the reactor (Figures 4, S1) and expanded in a jet-like fashion with a significant drop in average velocity along the tube length, (for example, from ~180.5 ms$^{-1}$ to ~2 ms$^{-1}$ over a length of 13 cm along the tube axis). This velocity decrease introduced an adverse or positive pressure gradient in this region, and, it could be observed that the boundary layer (BL) had detached itself from the tube wall and a recirculation zone had developed. Right next to the inlet, this recirculation zone almost completely filled the tube, and, as the jet of gas expanded further down the tube, the spread of the recirculation zone across the tube decreased till the BL reattached itself to the tube walls. Again, in this region, large values of vorticity $\xi$, $k$, turbulent viscosity $\nu_t$, specific dissipation rate $\varepsilon$ and $Ti$ were observed around the middle of the tube. The average $Ti$ in the entrance region was ~18% i.e. a high turbulence intensity. All turbulence variables were found to gradually decrease farther downstream.

At the end of the recirculation zone, the BL reattached itself to the tube walls and started growing to fill the tube completely and towards a fully developed turbulent flow. The line profiles of $k$, $\varepsilon$ and $Ti$ across the tube diameters in Figures 4, S1 showed expected trends: two symmetric
peaks on the two sides of the centerline, while large $\zeta$ values (Figure S1) were now confined to the BL regions next to the tube walls. The $U_{magnitude}$ across the tube diameter had a turbulent velocity profile that was mostly flat across the tube with a steep decrease to zero at the walls. The turbulence variables $k$, $\nu_t$, $\varepsilon$ and $Ti$ continued to decrease further as turbulence in the flow gradually decreased and the flow transitioned from turbulent to laminar. On the other hand, a slow increase in $U_{magnitude}$ along the tube axis was observed as the reactor tube was not long enough for the flow to develop fully.

Flow Dynamics in a Tube Reactor with a Suspended Copper Foil at Room Temperature

In a separate simulation, the flow around a 100 μm copper foil when the reactor was at RT was studied (condition T0, Table S3). The 2 cm long and 4 cm wide foil (foil setup A, Figure 3) was positioned downstream to the re-circulation zone, centered at 0.6 m from the inlet (as it would be in graphene growth experiments described later, and, in the Methods section). This meant that the foil was freely suspended in the bottom half of the tube, centered at a $y$ value of -0.0109 m. The flow was modified as expected when the foil was introduced into it and two new regions were formed: a new BL region around the foil and a wake region downstream to the foil (Figure S2). A stagnation line could be observed at the upstream edge of the foil, above and below which the fluid was deflected away from the foil. The BL region was also turbulent like the rest of the flow and increased in thickness (up to ~5-6 mm) from the upstream to the downstream edge of the foil. Thus, $U_{magnitude}$ showed stronger gradients normal to the foil at the upstream edge than at the downstream edge. The wake region was also turbulent, ~1 cm long, and, gradually merged with the rest of the flow. No adverse pressure gradients or any resultant BL separation or flow recirculation were observed, possibly because of the extreme thinness of the foil.
Measuring the Thermal Profile of the Tube Reactor

For simulating the heated reactor tube, the temperatures of the wall of the tube at various positions had to be measured (the furnace set-point by itself was insufficient for this). More specifically, this was the thermal profile of the inner wall of the tube, as the process was exposed to this wall (while the outer wall of the tube was exposed to the furnace and controlled by the furnace set-point). In order to ascertain the temperature of the inner wall of the CVD tube, the temperature inside the CVD tube was first measured from the center to the edge of the hot-zone under vacuum, using a thermocouple thermometer (TC), with the furnace set-point at the graphene growth temperature i.e. 1323 K (Figure S-T4). ‘Vacuum’ in this work means a system pressure below 0.1 torr, the lowest pressure that can be read by the specific baratron gauge used. The rationale for this set-up is that, as the TC was very close to the inner wall, and, as there was no cooling due to any flow of gas, the TC temperature must be approximately the same as the inner wall temperature at that position (this has been validated, please see SI for details). This measured data was then fitted (Figure S-T5) to obtain thermal profile A. This thermal profile A was used as a fixed value BC for the tube wall for all subsequent simulations of processes with the same furnace set-point.

Flow Dynamics and Temperature Distribution of a Hot, Empty Tube Reactor

For simulating the heated empty tube (condition T1, Table S3), the furnace was centered at 0.6 m from the tube inlet, at -0.15 m (like in a graphene growth experiment, Figure 3); thus, the center of the ‘hot-zone’ of the reactor tube was also at this position. Ar gas has a Prandtl number (Pr) of 0.67. A turbulent Prandtl number (Pr_t) of 1.0 was used for this and all other heated tube simulations, in accordance to Reynolds analogy (also see SI, P18). Thermal profile A started right from the inlet (at ~307 K) and continued for ~1.2 m downstream. The fluid temperature also
started increasing right after the inlet, and was greater than RT within the first 1 cm from the inlet. Similar to the tube at RT, a recirculation zone was also observed next to the inlet. There was almost no change in the values of the different flow variables in this part of the tube, possibly because the average temperature of the fluid, ~308 K showed only a small rise from RT. Further down the reactor, as the wall temperature increased further, the gas temperature increased, its density decreased and gas velocity increased. The wall temperature increased up to -0.15 m (i.e. up to the center of the hot zone) and then started decreasing; heat flow into the fluid could be observed with $T_{\text{wall}} > \text{gas } T_{\text{average}}$ till ~0 m (i.e. slightly downstream to the hot-zone center). Beyond ~0 m, gas $T_{\text{average}} > T_{\text{wall}}$ as a result of advection, and, the wall thus became a heat sink; near the outlet, $T_{\text{wall}} ~293$ K while gas $T_{\text{average}} ~463$ K. All flow properties were dictated by this thermal field; regions of high $T$ had lower densities and higher velocities (as mass flow rate i.e. $\rho*U*\text{Area}$ across the tube cross section must be conserved). Regions of higher $T$ also had higher values of dynamic and kinematic viscosities; all these changes resulted in lower $Re$ and decreased turbulence. For example, a 2 cm long region around the center of the hot-zone now had a $Ti$ of ~2.15%, compared to ~6.19% when it was at RT. Similarly, all other turbulence variables were modified by this thermal field with lower values of $k$ and $\nu_t$ at higher temperatures (Figure S3).

*Flow Dynamics and Temperature Distribution of a Hot Reactor with a Suspended Copper Foil*

Conjugate heat transfer simulations were then performed to calculate the temperature distribution across the 100 μm thick copper foil positioned at the center of the hot-zone (foil setup A and condition T1, Table S3). This was a multi-region simulation that calculated the temperature distribution across the foil. The edges of the foil touching the walls of the tube were at the same temperature as the tube-wall (this was provided as a fixed-value BC) while the central part in-between was calculated to be at relatively lower temperatures (Figure S4, a parabolic
profile could be observed along the foil width at a specific $z$ value). Again, the upstream edge of the foil was found to be colder than the downstream edge (Figure S4, an exponential increase in temperature could be observed from the upstream to the downstream edge along the foil centerline). Thus, the foil had an overall temperature range of $\sim 1202.51 - 1293$ K, with an average temperature of $\sim 1245.54$ K. In contrast, temperatures were found to be uniform through the foil thickness and the top and the bottom surfaces had similar temperature distributions. Temperature gradients calculated for the foil showed higher gradients for lower temperature regions that experienced a greater cooling effect by the flow of gas.

With respect to the flow, the recirculation zone upstream to the foil remained identical to the previous simulations. The BL region of the hot foil could now be described in terms of both the momentum and the thermal BLs (Figure S5). In the thermal BL, the temperatures of the gas in contact with the foil were the same as the foil and gradually changed to the values of the surrounding gas. The thermal and momentum BLs had thicknesses that ranged up to $\sim 6$ mm and $\sim 8$ mm respectively (the $Pr$ of 0.67 for Ar meant a thermal BL that was slightly thicker than the momentum BL). The thermal BL also increased in thickness from the upstream to the downstream edge of the foil, like the momentum BL and this was reflected in the higher temperature gradients at the upstream edge. Both the BL and wake regions were turbulent. The average gas temperature around the hot-zone center (i.e. around the foil) was only slightly higher (by $\sim 10$ K) than that of the heated empty tube (Table S4); hence, turbulence variables were also very similar. Hence, line profiles along the $x$ and $y$ diameters of the tube for $k$, $u_1$, $\varepsilon$ and $T_1$ in the hot zone were more like those of the hot empty tube than those of the tube with foil at RT. Thus, it may be concluded that introducing the copper foil to the heated tube produced only minor changes to its flow and thermal fields (Table S4).
The contributions of the different heating modes of the foil, namely, conduction, convection, and radiation, were explored with the 100 µm Cu foil. Accordingly, different control experiments were simulated (Table S5) where a heating mode was artificially deactivated. It was observed that when the effects of radiation were not considered (control H1), foil temperatures barely decreased, owing to the low thermal emissivity of copper. When the foil edges no longer touched the hot tube wall but had a small gap of 2 mm (i.e. heat conduction from the tube wall to the foil was no longer possible, control H2), the foil average temperature decreased by ~267 K. When the foil touched the tube wall only partially, its temperature was still lower than the default case, but by much smaller amounts (control H3: ~27 K, control H4: ~23 K). Finally, when the gas velocity was reduced (i.e. minimal convection, by using a very small mass flow rate at the same system pressure, control H5), the foil temperatures were nearly equal to the tube wall temperatures. (In all these cases, the average temperatures of the fluid around the foil at the center of the hot-zone were in a similar range, around ~738 – 739 K, while being slightly lower for control H2 (~713 K) and much higher for control T5 with a negligible gas flow (~1292 K)). Thus, the temperature of the copper foil was primarily driven by heat conduction (heating) and convection (cooling). Increased conduction was found to increase the foil temperature while a reduction in convection reduced cooling due to gas flow and hence also increased the foil temperature. This also implied that any changes in the flow conditions (gas velocity and system pressure) as well as foil position (whether and by how much it touches the tube wall) will possibly modify the temperature field of the foil.

Part 2. Exploring ‘Real’ Graphene Growth Experiments
As mentioned on P5-6 (as well as the ‘Methods’ section and Figure S-T1), SLG films were grown in our system from an Ar-H₂-CH₄ mix on 50 μm thick Cu(111) foils.

*Simulating the Graphene Growth Process*

The process gases Ar and H₂ in the reactor around the foil mixed completely due to the significant turbulence present in the pipelines and the recirculation zone at the reactor entrance upstream to the foil. Changing the gas composition to the actual Ar-H₂ mixture (1.23% H₂ by mass, 19.65% by moles, **condition A**) produced thermal fields that were similar to the ones with **condition T1** discussed above (Figures 5, S6). The transport equation of the passive scalar CH₄ was then solved. For obtaining the concentration profile of CH₄ in the reactor, the concentration of CH₄ was assumed to be 0.0 on the foil surface, implying that CH₄ was converted into forms of C (like atomic C that eventually forms graphene on the foil surface) and/or other ‘CH’ fragments ‘instantaneously’ on contacting with the catalytic foil. The copper foil acts as a sink for CH₄, but as only a CH₄ amount equivalent to a C film that is one atomic layer thick is extracted from the flow, this amount is extremely small and hence, can be neglected for calculating flow properties. The CH₄ distribution around the foil is shown in Figures 5, S6. The concentration BL for CH₄ was thinner and with higher gradients at the upstream edge than the downstream edge, like for the thermal and momentum BLs. (Distributions around a 100 μm Cu foil were found to be similar, please see Figures S7, S8). The SLG film thus synthesized was a continuous single crystalline film, with no carbon adlayers (Figure 1). From its Raman spectra, it was confirmed that this was a high quality SLG film (Figure S9).

*Factors Affecting the Reaction Environment*

The changes in the flow conditions and the thermal profiles of foil and gas (i.e. the reaction environment around the foil) when external parameters such as the foil thickness, system pressure,
The Effect of Foil Thickness

The foil thickness in the simulations discussed so far are 50 or 100 μm, while in typical graphene growth experiments the thickness may range from 25 – 100 μm. In order to understand how foil thicknesses may affect their temperatures, simulations were performed for a range of foil thicknesses (with foil setup A and condition A, Table S6, Figure 6). It was observed that as the foil thickness increased, both the minimum and the average foil temperatures increased. Moreover, the temperature distribution was much more uniform with smaller temperature gradients, for increasing foil thickness. Interestingly, even for a 1 mm thick foil, the top and the bottom surfaces had the same temperature distributions (Figure S10). In comparison, fluid temperatures remained almost the same. This trend was also observed for flow conditions other than condition A (Table S6). This increased sensitivity with decreasing thickness is possibly due to a decreasing thermal mass and a decreasing absolute area of contact between the foil and the hot tube wall while the same foil area was exposed to the flowing process gases. This implies reduced heating by conduction but similar amounts of cooling due to convection. This could possibly be an important criterion to consider when designing processes as well as analyzing chemical kinetics data.

The Effect of Process Gas Composition: The Role of H₂

In order to understand the effect of H₂ gas on flow properties, two total mass flow rates (229 sccm and 79 sccm) were studied, with different proportions of H₂ (with foil setup A, Table S7, Figure 7 and Figure S11). It was observed that with an increasing proportion of H₂, the fluid was hotter, with higher values of minimum and average temperatures around the foil in the hot-
zone. In fact, for the H\(_2\) only flow, the fluid temperatures in the hot-zone were found to be very close to the temperatures of the reactor wall. In comparison, foil temperatures were similar or higher (by smaller amounts than for the gas) than for the Ar only flow at the same mass flow rate. Again, the \(Ti\) in the fluid around the foil also decreased with higher amounts of H\(_2\) in the mix, owing to its higher temperatures. Additionally, increased temperatures in the BL regions meant increased diffusion of CH\(_4\) and thicker concentration BLs for CH\(_4\) around the foil. The possible cause for increased temperatures with H\(_2\) is its \(\sim\)10 times higher thermal diffusivity compared to Ar. Hence, such an increase in temperature could also be an important criterion to consider during process design and while interpreting previously reported processes and chemical kinetics data.

Most gas mixtures for graphene growth are either H\(_2\) rich (i.e. a mixture of H\(_2\) and a carbon precursor are used) or contain significant amounts of a chemically inert gas (typically Ar or N\(_2\)); in the former case, actual fluid and foil temperatures in the center of the hot-zone may well be very close to the furnace set-point.

The Effect of Process Gas Composition: The Role of Ar

Finally, the role of ‘excess’ Ar that had been used for graphene growth, in addition to H\(_2\) and diluted CH\(_4\) (with foil setup A, Tables S8-S9, Figures 8, S12 for the 50 \(\mu\)m foil and Figure S13 for the 100 \(\mu\)m foil) was explored. For example, condition A that produces high quality SLG had an excess of 150 sccm Ar, in addition to 45 sccm H\(_2\) and 34 sccm of diluted CH\(_4\). It was observed that, (for both the 50 \(\mu\)m and the 100 \(\mu\)m foils) there was a decrease in both the fluid temperatures and the foil temperatures with increasing amounts of excess Ar gas. The decreases in foil temperatures were comparatively smaller and the lowest calculated foil temperatures ranged from \(\sim\)1169 – 1293 K (average: 1228 K) for the 100 \(\mu\)m foil and from \(\sim\)1089 – 1293 K (average: 1186 K) for the 50 \(\mu\)m foil (for the case with 300 sccm of excess Ar). In comparison, gas average
temperatures in cases with either foil were around or less than 773 K for excess Ar amounts greater than 150 sccm. Specifically, the BL regions around the foil were found to be much hotter and thicker when excess Ar amounts were lower than 25 sccm, in comparison to flows with excess Ar greater than 150 sccm. Consequently, concentration BLs for CH₄ were also thicker at these lower amounts of excess Ar (Figures S14, S15).

In order to explore this further, graphene was grown on 50 μm copper foils with different amounts of excess Ar. It was observed that, in addition to an excess Ar amount of 150 sccm (condition A), 300 sccm of excess Ar also produced pristine SLG films. In comparison, no excess Ar or a small amount of 25 sccm of excess Ar produced SLG with adlayers (Figure 1). This suggests that SLG is obtained when the foil is sufficiently hot while the surrounding gas is relatively cold, as might be found in a cold-wall reactor.

The ratio of H₂:CH₄ is known to be critical for graphene growth, possibly because (1) H₂ reacts with CH₄ (in the gas-phase and on the Cu surface) and produces active species that react with Cu to form graphene while also (2) etching graphene films on the Cu surface.³² Thus, the fact that a SLG film with adlayers was obtained on increasing the mass flow rate of H₂ by 10 sccm from condition A could be considered to be an effect of changing chemical reactivity due to a modified H₂:CH₄ ratio, as flow properties do not change in this scenario. On the other hand, SLG with adlayers was obtained when all mass flow rates of condition A were reduced by one-third (Figure S16). In this case, the same H₂:CH₄ ratio was maintained while the flow and foil properties changed (were hotter) owing to considerably lower mass flow rates. Again, for the examples discussed in the preceding paragraphs (Tables S8-S9), the H₂:CH₄ ratios had remained the same while flow and foil properties were modified by the amount of additional Ar. This
suggests that a hotter, thicker BL may facilitate (1) that leads to the formation with SLG with adlayers.

All of the above findings seem to indicate that (1) SLG is formed at an optimum H$_2$:CH$_4$ ratio that (2) changes with temperature. This suggests that multiple windows for synthesizing SLG films are possible where the H$_2$:CH$_4$ ratios have to be optimized for specific temperature ranges. 

*Caveat: How ‘exact’ are the Simulation Results?*

Though the calculations discussed above provide a very good picture of what might be happening inside the reactor at different settings of its controllable external parameters and a great indication of different trends, the calculated values are not exact. Potential errors may arise due to a range of factors such as uncertainties in material properties (like thermal conductivity or emissivity values), measurements (system pressure and temperature), the extent to which the copper foil touches the reactor walls in a real experiment (this is likely to vary from one experiment to another) or approximations used in the CFD calculations. At this point, there is no direct method to measure the foil temperatures in a hot-wall reactor. For example, our attempts to measure the foil temperatures with a pyrometer were unsuccessful as the latter always recorded the temperatures of the hotter heating elements of the furnace instead. In comparison, temperatures could be measured by a TC inserted inside the reactor and matched against simulated data, when no gas was flowing (as discussed on *P10* and the *SI, P14*). However, the TC temperatures do not change appreciably under different mass flow rates or system pressures owing to the large thermal mass of the TC and hence the utility of this method was limited.

**Conclusion**

In this paper, we have described (1) our exploration of the synthesis of adlayer-free and single-crystalline SLG on copper foils by combining experimental and simulation data; to the best
of our knowledge, it is the first such systematic study for the growth of graphene and other 2D materials. Again, to the best of our knowledge, this is also the (2) first example of the use of CFD modeling with OpenFOAM for studying the CVD synthesis of graphene. We have found that (3) the tube reactor, typically used in the laboratory synthesis of graphene, operates under turbulent flow conditions (and that this reactor must be studied as a part of the entire CVD system that includes the gas pipelines after the MFCs and upstream to it). We have also found that (4) the copper foil temperature is not uniform and very sensitive to the process gas composition, their mass flow rates and system pressure owing to its very small thickness (< 100 μm): this has important implications for designing experiments and studying growth kinetics. Finally, we have found that (5) the best condition to grow pristine adlayer-free SLG films in our CVD system is when this hot-wall reactor becomes cold-wall like, with the foil temperatures sufficiently hot to grow graphene but the average gas temperatures remaining relatively cool (~773 K or less) so that gas phase reactions are minimized. This work provides a glimpse into how experimental data can be effectively supplemented with CFD modeling to understand the graphene growth process, and, improve process repeatability and reproducibility.
Methods

Graphene Growth. In a typical process, a “home-made” Cu(111) foil,\textsuperscript{24} 50 μm thick, ~4 cm wide, and, ~2 cm long was placed inside the reactor (such that its two short edges were in contact with the quartz tube, and its two long edges were freely suspended, along with its top and bottom surfaces) inside the reactor, at a distance of 60 cm from the inlet (foil setup A, Figure 3). The reactor pressure was set to 100 torr at the outlet. The furnace temperature was ramped to 1323 K (the furnace set-point) under a flow of Ar (150 sccm) and H\textsubscript{2} (45 sccm). Once at the final temperature, a flow of 34 sccm of diluted CH\textsubscript{4} (0.1% CH\textsubscript{4} in Ar, by moles) was introduced for 1 h (condition A, Figure S-T1). At the end of the growth process, the furnace was turned off and quickly moved away from the foil (as the furnace is on a rail system, sliding it was straightforward). The foil was then rapidly cooled to RT, aided by a table fan. All process gases were of an ultra-high purity (99.999\%) grade that were further purified with respect to possible oxidants like O\textsubscript{2} and H\textsubscript{2}O by respective gas-purifiers. Additional details about the reactor and process set-up can be found in the SI.

Graphene Characterization. The as-synthesized graphene films were characterized by SEM (Verios 460), AFM (Bruker Dimension Icon System), and, Raman spectroscopy (WiTEC instrument using a 532 nm laser and 600 g/mm or 1800 g/mm gratings).

CFD Simulations. All simulations were performed using OpenFOAM and the solvers utilized include: buoyantSimpleFoam (for gas only cases), chtMultiRegionSimpleFoam (for multi-region cases) and a modified scalarTransportFoam (for solving transport equations for passive scalars in the flow). All equations, models used, BCs and other relevant details can be found in the SI.
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References


Advanced materials (Deerfield Beach, Fla.) 2019, 31 (35), e1903615. DOI: 10.1002/adma.201903615. Published Online: Jul. 2, 2019.

(23) Robert B. White; D. King. COMBINED EXPERIMENTAL AND SIMULATION (CFD) ANALYSIS ON PERFORMANCE OF A HORIZONTAL TUBE REACTOR USED TO PRODUCE CARBON NANOTUBES 2009.


Figure 1. SEM images of (A) pristine single layer graphene films (‘good’ SLG), and (B) single layer graphene films with adlayers (‘bad’ SLG).
Figure 2. Reactor conditions discussed; orange: both graphene growth and simulation data; blue: simulations only. The boundary conditions for all simulations are based on data measured from our CVD system.
Figure 3. (A) Schematic of the CVD system for graphene growth; (B) geometric depictions of the reactor tube and foil, showing their dimensions and orientations: (1) inlet, (2) door, (3) suspended foil, (4) tube wall, (5) outlet; (6) upper half, and, (7) lower half of the reactor tube; (8) upstream, and, (9) downstream edges of the foil; (10) bottom, and, (11) top surfaces of the foil; L: length, W: width, and Th: thickness of the foil. Line * shows the y diameter of the reactor tube that cuts through the foil and have been used for extracting several line profiles discussed in the paper. All axes are in m.
Figure 4. Flow inside an empty reactor tube with a flow of 229 sccm of Ar at 100 torr and RT (condition T0): (A) YZ slice (axes in m, at x = 0 m) of the tube showing streamlines near the inlet (color coded with $U_z$); line profiles across the tube y diameter (m) at x = 0 m, and, (B) $z = -0.7$ m (entrance region), and, (C) $z = 0.6$ m; (D) along the tube axis (m). $U_z$ is in m s$^{-1}$, $k$ is in m$^2$s$^{-2}$, $\nu_t$ is in m$^2$s$^{-1}$, and, $\varepsilon$ is in m$^2$s$^{-3}$.
Figure 5. (A)-(C) Line profiles along the tube y diameter (m) at $x = 0$ m and across a 50 μm foil (with setup A and condition A) at $z = -0.159$ m (US, close to the foil upstream edge), at $z = -0.15$ m (C, at the foil center), and, at $z = -0.141$ m (DS, close to the foil downstream edge) for fields (A) $\text{mag}(U)$ (ms$^{-1}$), (B) $T$ (K), and, (C) normalized $\text{CH}_4$ concentration. (E)-(K): slices of the tube showing $\text{mag}(U)$ (ms$^{-1}$) and $T$ (K) fields of the process gases, and, normalized methane concentration ($s$) around the foil: (E)-(G) $YZ$ slice (at $x = 0$ m), (I)-(K) $XY$ slice (at $z = -0.15$ m) of
the reactor tube, with all axes in m. (L) and (M) show the $T$ (K) and $\text{grad}(T)$ (Km$^{-1}$) on the foil surface (axes in m) respectively. (N) Line profiles across the width (m) of the foil (along $x$) at $z = -0.159$ m (US), $z = -0.15$ m (C), and, $z = -0.141$ m (DS) through the middle of the foil (at $y = -0.0109$ m). (O) Line profile along the foil length (m) showing an exponential increase in $T$ from upstream to downstream edge of foil (along $z$) through its middle (at $x = 0$ m, $y = -0.0109$ m). Arrows indicate foil location.
Figure 6. (A)-(B): Variation in $T$ (K) with foil thickness for (A) foil, and (B) gas temperatures. (C)-(F) show the foil surface (axes in m) $T$ (K) for 50 μm (C), 100 μm (D), 200 μm (E), and, 1 mm (F) thick foils.
Figure 7. (A)-(C) Line profiles along the tube y diameter (m) at $x = 0$ m and across the center (at $z = -0.15$ m) of the 100 μm foil (with foil setup A) for flows with different mass% of H$_2$: (A) $\text{mag}(U)$ (ms$^{-1}$), (B) $T$ (K), (C) normalized CH$_4$ concentration. (D)-(H): YZ slices (axes in m, at $x = 0$ m) through the reactor tube showing the gas $T$ (K) fields around the foil with (D) an Ar only flow, flows with (E) 1%, (F) 10%, and, (G) 15% H$_2$ and, (H) a H$_2$ only flow. Arrows indicate foil location.
Figure 8. (A)-(C) Line profiles along the tube $y$ diameter (m) at $x = 0$ m and across the center (at $z = -0.15$ m) of the 50 μm foil (with foil setup A) for different amounts of excess Ar (sccm): (A) $\text{mag}(U)$ (ms$^{-1}$), (B) $T$ (K), (C) normalized CH$_4$ concentration. (D) and (E) show the variation in foil and gas $T$ (K) respectively, with different amounts of excess Ar. (F)-(G): YZ slices (axes in m, at $x = 0$ m) through the reactor tube showing gas $T$ (K) around the foil for different excess Ar amounts: (F) 79, and, (G) 379 sccm. (H)-(I): Foil surface (axes in m) $T$ (K) under an excess Ar amount of (H) 79, and, (I) 379 sccm. Arrows indicate foil location.