Deposition of few-layered graphene in a microcombustor on copper and nickel substrates

Benjamin M. Kellie, Alexander C. Silleck, Karen Bellman, Ryan Snodgrass and Shaurya Prakash*

Carbon nanomaterials, including few-layered graphene (FLG), were synthesized on high-purity copper and nickel wires in a microchannel within an alumina microcombustor with a methane/oxygen edge flame. The deposition occurred in 20 s with identifiable FLG Raman peaks. The FLG layers were characterized by Raman spectroscopy and scanning electron microscope (SEM) imaging. The data shows 5–8 layers can be formed on the wires in a microchannel. The versatility of the microcombustor platform for rapid deposition of carbon nanomaterials is also shown through demonstrations of formation of near-perfect graphite thin films.

Introduction

Interest in carbon materials such as graphene, a one atom thick graphite layer, is high because of unique properties such as the high charge carrier mobility of 15 000 cm² V⁻¹ s⁻¹,¹,² which makes it ideal for use in electronic devices and biosensors.³ In addition, strong structural properties show promise for use in composite materials.⁴,⁵ Additional interest has been generated in the synthesis of carbon nano-ribbons, diamond,⁶ and highly ordered pyrolytic graphite (HOPG). Nano-ribbons are of interest due to the relative high yield synthesis that has been shown experimentally.⁷ HOPG has generated interest due to the ease in which small amounts of graphene can be obtained via exfoliation of HOPG.⁸ As a result, research activity in the area of graphene synthesis has been high and many approaches have been investigated to form graphene films, including computational analyses.⁹,¹⁰ One of the earliest experimental methods used, mechanical exfoliation of graphite, allowed for the isolation of graphene flakes.¹¹ However, this method is not scalable for engineered device production as the mechanically exfoliated flakes are irregularly shaped and the size is variable but on the order of few microns.¹² Eda et al. have shown a pathway to large-area thin films through the reduction of graphene oxide flakes which are separated and controlled through a solution filtering process.¹³ Previous approaches utilizing chemical vapor deposition (CVD) have been shown to be effective for producing few- and mono-layer graphene films with ability to scale-up for production at large scales, but require large chambers sealed against the outside atmosphere, high vacuum, multi-step processes, and exhibit low process efficiencies, at 15% or lower.¹³–¹⁵ Effects of gas composition, metal substrate type, and deposition temperature conditions have also been explored.¹⁶–¹⁸ Graphitization of silicon carbide¹⁷–¹⁹ as an alternate method of synthesis has also been demonstrated. Typically, all these methods require deposition time of several minutes to hours and fine control over deposition conditions.¹³,²⁰,²¹

Alternatively, fast throughput methods have also been considered, such as using flame deposition of carbon materials. Flame synthesis of carbon nanotubes has been demonstrated previously.²² It has also been shown that few-layered graphene (FLG) films can be created on nickel (Ni) foils using a dual-flame alcohol burner in open environments;²³ however, no explicit discussion of the number of layers deposited was presented. In another flame deposition report, FLG film generation on Ni and Cu utilizing a methane/oxygen diffusion flame doped with hydrogen²⁴ showed a deposition of 5–8 layers in a combustion chamber over a 30 minute period. In both flame deposition methods the flames (and subsequent post-combustion gases) were directly impinging on the Ni or Cu foils, creating a standard stagnation flow arrangement characteristic of flame studies.²⁵

Previous work on microcombustion has led to development of sub-millimeter or microcombustors with extensive flame structure studies²⁶–³¹ including descriptions for stability of flames and need for surface modification to control substrate properties.²⁵,³²,³³ While most work on microcombustors has been targeted at developing portable power or energy systems,³⁴–³⁸ other applications include use as micro-flame ionization detectors.³⁹ Past work²⁵,²⁷,³¹ has shown that the mixing for laminar flames within microcombustors is not limited to the molecular diffusion region due to sharp gradients in temperature and density driving convective eddies.
enhancing local mixing. Overall, the combustion efficiency can be systematically controlled and further enhanced, even though that is not the objective of this work. In this paper, microcombustion is applied for materials synthesis for the first time, in which the microcombustor is used as an integrated heat source and reactor for deposition of few-layered graphene (FLG) on Cu or Ni wires within the boundary layer region over the wire by using the post-combustion gases in the microchannel. The purpose of this paper is to report on an approach to FLG synthesis that is rapid with deposition in 20 s, for local deposition applications, and potentially scalable through the implementation of device arrays after further work for a variety of potential applications.

Experimental

The carbon source for graphene synthesis is generated by a "Y-shaped" alumina microcombustor fabricated previously by the Prakash group. Briefly, the microcombustor was fabricated with channel size 1.1 mm × 0.8 mm (W × D) machined into a 5 cm × 5 cm × 0.6 cm (L × W × D) alumina block. After fabrication of the microcombustor, it was sealed with a quartz top (Fisher Scientific, #CGQ-0620-07) using an alumina based adhesive (Ceramabond 671 Aremco, Inc.) to enable flame imaging during deposition. Alumina tubes (McMaster Carr, #8746K451) were then attached to deliver fuel and oxidizer to the microcombustor. High purity methane (99%) and oxygen (99.6%) were utilized as the fuel and oxidizer, respectively. The flame is initially ignited at the outlet of the microcombustor, and stabilizes to a continuous edge-flame anchored at the stagnation point, as shown previously. Fig. 1 shows a digital photograph of the microcombustor in operation. A Cu or Ni wire with 0.5 mm diameter (Alfa Aesar, 99.98% purity) was placed inside the sealed microchannel just beyond the visible end of the flame. The inlet fuel and oxidizer ratios were varied between 1.0 and 2.9 through mass flow controllers (Type 1179A, MKS Instruments). The range of volumetric flow rates used translates to an incoming velocity of 3.7 m s⁻¹ to 9.9 m s⁻¹ for CH₄ and 1.5 m s⁻¹ to 7.4 m s⁻¹ for O₂. It should be noted that the flows were laminar with Re <100 with gas properties estimated at 800 K, based on previous reports of microcombustion in a similar configuration.

External wall temperature data was also recorded (not shown explicitly in this paper) through a computer controlled data acquisition set-up similar to previous flame structure studies for microcombustion along the length of the exhaust outlet over the metal wire substrate. Before placing the wires in the microcombustor, the wires were cleaned by rinsing in acetone followed by DI water, IPA, and DI water again to remove any organic contamination, and then dried using filtered dry air. All results reported here were for a 20 s exposure of the wire to post-combustion gases in the microchannel. It should be noted that a deposition time between 5 s to 5 min. was evaluated. As discussed in the results section, deposition shorter than 20 s led to unreliable deposition and for deposition greater than 20 s, the continued carbon layer depositions usually led to formation of bulk graphite or soot in some cases. The microcombustion assembly was insulated using an alumina-foam insulation similar to previous work.

Results and discussion

Deposition on nickel

A broad range of inlet fuel/oxidizer ratios were tested as discussed in the experimental methods section. However, only some conditions yielded carbon deposition on the Ni wire. As oxygen content in the inlet gas mixture was increased, the Ni wires were found to oxidize and inhibit deposition of carbon within 20 s. Longer depositions conditions (>30 s and reaching 5 min.) were tested but yielded deposition of soot. Next, specifics of FLG layers for Ni deposition are discussed.

Previous reports of FLG show that full width at half maximum (FWHM) of 75 cm⁻¹ was observed for the 2D peak. In addition, the ‘D’ peak at 1350 cm⁻¹ is considered to be a marker of the disorder in the graphene layers. In previous reports, a peak intensity ratio between the G and 2D peaks (I_G/I_2D) has been used to estimate the number of layers present in FLG. A ratio of 2.4 was considered to yield 10 layers and FLG with greater than 10 layers was considered to approach bulk graphite. In the data reported here, the lowest I_G/I_2D ratio was measured to be 4.6 at an inlet equivalence ratio of 2.4 (flow rates of 236 sccm CH₄ and 100 sccm O₂). Therefore, for deposition on Ni, the number of FLG layers was greater than 10 and can be considered approaching bulk graphite. An SEM image of the carbon layers deposited in the microcombustor on Ni wires is shown in Fig. 2.

Deposition on copper

Copper is known to yield better graphene films with CVD deposition in contrast to Ni wires due to lower solubility of carbon in Cu. Therefore, for microcombustor deposition, Cu
wires were considered next. Since an inlet equivalence ratio of \( \sim 2.4 \) yielded the fewest layers of carbon with the possibility of approaching FLG based on Raman data on Ni, the condition was used as a starting point for deposition on Cu wires. Previous reports on graphene quality have used peak intensity ratios and peak widths as markers to quantify degree of disorder and number of layers of graphene deposited.\(^{24,46}\) As the total inlet flow rate was increased from 336 sccm to 756 sccm (beyond which the edge-flame is no longer stable\(^{27,29,31}\)), an increasing intensity in the 2D peak was observed. At the maximum total flow rate of 756 sccm the 2D peak has a FWHM of 150 cm\(^{-1}\). Furthermore, no D peak was detected at the highest total flow rate of 756 sccm, suggesting highly ordered films as shown in Fig. 3. In contrast, previous work using Raman spectroscopy has reported an \( I_D/I_G \) ratio of 0.35 to quantify the degree of disorder in the FLG films.\(^{24}\) Previous work has also confirmed these results through atomic force microscopy and shown the \( I_{2D}/I_G \) ratio to be an effective measure of number of layers and sample thickness.\(^{23,45}\) Therefore, using these previous reports, using the peak intensity ratio to determine the number of layers is a viable approach, and was also used in the results reported here.

Fig. 4 shows changing the oxidizer content in the inlet gas stream by 5 or 10 sccm alters the Raman spectra with the 2D peak being suppressed as the oxidizer content is increased to 230 sccm. As the oxidizer content was reduced to 215 sccm the D peak re-appears (the \( I_D/I_G \) ratio of 0.55) and the 2D peak broadens from approximately 150 cm\(^{-1}\) to more than 200 cm\(^{-1}\).

Table 1 summarizes the ratios between the D and G peak intensities (\( I_D/I_G \)) as well as the ratios between the G and 2D peak intensities (\( I_G/I_{2D} \)). It can be seen in Fig. 5 that above the total flow rate of 336 sccm the D peak was no longer detected, suggesting lack of disorder in FLG layers. The \( I_{2D}/I_G \) peak ratio for the 756 sccm case shows that between 5–8 layers of FLG can be deposited in the microcombustor at Reynolds number (\( Re \)) approaching 90 within 20 s. When compared with the results for Ni deposition, this data indicates FLG on a Cu substrate displays a higher level of order than FLG on a Ni substrate.

It should be noted that the geometry of deposition here is not an impinging jet flow on the substrate as is common in most flame deposition studies. Given use of the distinct deposition configuration, carbon deposition along the length of the wire was also evaluated. The boundary layer deposition permits a local gradient in temperature and species concentration over the wire in the stream wise direction. It is hypothesized that the boundary layer gradient plays a dominating role in the carbon species that are seen along the length of the wire. It was previously shown that a temperature gradient of \( \sim 29^\circ\text{C cm}^{-1} \) exists along the length of the microchannel.\(^{31}\) As the deposition and probing length is on the order of 200 \( \mu \)m, the temperature gradient is expected to be \( < 1^\circ\text{C} \) over the 200 \( \mu \)m deposition and probing length. Consequently, changes in solubility are likely negligible based

### Table 1 Summary of peak intensity ratios and Reynolds numbers for fixed inlet equivalence ratio of 2.4 for deposition on Cu wires

<table>
<thead>
<tr>
<th>Fuel (sccm)</th>
<th>Oxidizer (sccm)</th>
<th>( I_D/I_G )</th>
<th>( I_G/I_{2D} )</th>
<th>( Re )</th>
</tr>
</thead>
<tbody>
<tr>
<td>236</td>
<td>100</td>
<td>0.48</td>
<td>7.1</td>
<td>39</td>
</tr>
<tr>
<td>354</td>
<td>150</td>
<td>N/A</td>
<td>4.6</td>
<td>59</td>
</tr>
<tr>
<td>472</td>
<td>200</td>
<td>N/A</td>
<td>3.2</td>
<td>79</td>
</tr>
<tr>
<td>531</td>
<td>225</td>
<td>N/A</td>
<td>2.1</td>
<td>89</td>
</tr>
<tr>
<td>531</td>
<td>230</td>
<td>N/A</td>
<td>N/A</td>
<td>90</td>
</tr>
</tbody>
</table>
on the carbon-copper solubility diagram reported in the ASM Handbook as a function of temperature. Therefore, the different carbon forms deposited and quantified by Raman spectroscopy (see Fig. 6) arise not due to temperature gradients but likely due to the boundary layer deposition within the microchannel which likely drives a concentration gradient of radicals and other key species. It should be noted that the actual mechanism of deposition as presented by the hypothesis above will require extensive investigation, but is not the purpose of this paper and will consequently be explored in continuing research.

Fig. 6 shows that the carbon forms were highly ordered pyrolytic graphite down the wire (lack of D-peak was observed with spectra similar to previous reports of HOPG), with the exception of approximately 40 μm from the tip where FLG is present. An SEM of the FLG seen from these tests is shown in Fig. 7. It can be seen in Fig. 7B that FLG flakes of up to ~30 μm² have been deposited on the substrate. Additionally, no measurable carbon signal was detected beyond 200 μm on the wire for flow conditions of 756 sccm and inlet equivalence ratio of ~2.4.

The lack of a carbon signal beyond 200 μm is hypothesized to be due to the boundary layer extending through the entire available space in the microchannel. As the boundary layer thickness increases down the wire, it eventually becomes large enough to begin interactions with the microchannel walls. Note, estimating boundary layer thickness in a microchannel with reacting flows and local gradients in temperature and species is a research problem in itself, likely requiring extensive numerical modeling. In this paper, a flat plate solution was implemented by assuming the reaction is at 800 K with gas properties for methane and oxygen used at that temperature to provide a first-order approximation to the boundary layer thickness reaching over 100 μm on either side of a 500 μm diameter wire in a 800 μm deep microchannel.

**Conclusions**

Carbon nanomaterials, including few-layered graphene, were flame synthesized on both Ni and Cu wire substrates using an alumina microcombustor. The carbon layers were synthesized within 20 s using boundary layer deposition in a microchannel.

On Ni wire substrates more than 10 layers of disordered FLG were deposited. This is attributed to the increased solubility of the Ni substrate at high temperatures. On Cu wire substrates, the Raman data showed that 5–8 layers of graphene could be synthesized in 20 s at a flow rate of 756 sccm with an inlet equivalence ratio of 2.4. Furthermore, the D peak (~1350 cm⁻¹) was not present in the spectra, suggesting lack of disorder in the FLG films.

It was also shown that other carbon nanomaterials can be deposited on the Cu wires down the length of wire due to boundary layer effects on the flow in the channel. The microcombustor provides a platform for local deposition of carbon-based nanomaterials including FLG.
Acknowledgements

The authors acknowledge assistance from Christopher Steineman for sample preparation, Gordon Renkes of the Analytical Spectroscopy Laboratory, the staff at Nanotech West, and partial financial support for personnel from the National Science Foundation (NSF) through grant IIP-1046876. We note that this application of microcombustion is made possible because of the pioneering contributions of Prof. Mark A. Shannon at the University of Illinois towards the development of fundamentals in this area of science and technology, and so we dedicate this paper to a wonderful scientist, mentor, and leader.

Notes and references

5. B. Debalak and K. Lafdi, Use of exfoliated graphite filler to enhance polymer physical properties, Carbon, 2007, 45(9), 1727–1734.
15. F. Sarkozy, Method for Providing Substantially Waste-Free Chemical Vapor Deposition of Thin-Film on Semiconductor Substrates, United States patent, US 4,556, 584.


