Atmospheric Deposition of Modified Graphene Oxide on Silicon by Evaporation-Assisted Deposition

Kevin Gleason,† Shashank Saraf,§ Sudipta Seal,§⊥ and Shawn A. Putnam*†⊥

†Department of Mechanical Engineering and Material Science, Yale University, 10 Hillhouse Avenue, P.O. Box 208267, New Haven, Connecticut 06520, United States
‡Department of Mechanical and Aerospace Engineering and †Department of Materials Science and Engineering, University of Central Florida, 12760 Pegasus Blvd., P.O. Box 162450, Orlando, Florida 32816, United States
§Advanced Materials Processing and Analysis Center, University of Central Florida, 4000 Central Florida Blvd., P.O. Box 162455, Orlando, Florida 32816, United States
⊥Nanoscience Technology Center, University of Central Florida, 12424 Research Parkway Suite 400, Orlando, Florida 32816, United States

ABSTRACT: We present a deposition technique termed evaporation-assisted deposition (EAD). The technique is based on a coupled evaporation-to-condensation transfer process at atmospheric conditions, where graphene oxide (GO) is transferred to a Si wafer via the vapor flux between an evaporating droplet and the Si surface. The EAD process is monitored with visible and infrared cameras. GO deposits on Si are characterized by both Raman spectroscopy and X-ray photoelectron spectroscopy. We find that a scaled energy barrier for the condensate is required for EAD, which corresponds to specific solution–substrate properties that exhibit a minimized free energy barrier at the solid–liquid–vapor interface.

1. INTRODUCTION

Two-dimensional (2D) materials are of high interest for their promising advances in photovoltaics, thermal and mechanical improvements of ceramics, chemical vapor sensors, and field-effect transistors. Although graphene remains as the spotlight 2D material, recent efforts to extend to exploring additional materials such as MoS₂, WS₂, h-BN, and phosphorene introduces selective chemical functionality for applications in biosensors or energy conversion/storage and introduces a wide range of deposition techniques such as spraying, dip-coating (including Langmuir–Blodgett), and spin-coating. Substrate dip-coating methods have a broad range of benefits; however, the capillary flow of the liquid and solid–liquid–vapor contact line dynamics typically produce nonuniform deposits (i.e., the coffee-ring effect). Chemical vapor deposition (CVD) and physical vapor deposition (PVD) currently show great promise for industrializing 2D materials and can produce films on the order of square centimeters. Because of the need of a high-temperature environment for thermal CVD, material deposition is limited to specific material substrates. Therefore, additional stamping/lithography steps are required for depositing on arbitrary substrates. Although PVD and wave plasma CVD are low-temperature methods (low relative to thermal CVD, yet still ~400 °C), the material deposited is still vaporized because of the high vacuum conditions and any chemical functionality is lost. As a result, large-scale deposition of chemically derived graphene using CVD/PVD remains constrained to post-grown functionalization of graphene sheets.

The current work is a result of our efforts to find a method with the combined versatility of chemical functionalization with liquid exfoliated solutions and large-scale uniformity through vapor deposition methods—thus leading to our discovery of material deposition at near atmospheric conditions, which we term evaporation-assisted deposition (EAD). We achieve a vapor-phase-assisted mass transportation of a chemically modified graphene oxide (GO) at low temperatures (<100 °C) and atmospheric pressure such that the GO nanoparticles remain in the solid phase after crossing the liquid–vapor interface into the ambient gaseous environment. With growingly popular matrix-assisted mass spectroscopy for analyzing large nonvolatile proteins and other biomolecules, gas/vapor-
phase transportation becomes possible without fragmentation, preserving chemical functionality.

2. RESULTS AND DISCUSSION

The setup used for performing an EAD is shown in Figure 1a. A polymer acrylic substrate is fabricated to control the contact line dynamics of a droplet, and computer-controlled syringe pump maintains the droplet of a lightly sulfonated graphene oxide dispersion (LSG) in steady-state evaporation. Briefly, the polymer substrate is heated, and the flow rate into an evaporating droplet is controlled to maintain its volume (and all other droplet parameters) constant over an extended period of time. A target substrate for deposition (e.g., a Si wafer) is translated above this evaporating droplet. The target substrate is mounted onto a large thermal mass (heat sink) to maintain its temperature below the effective dew point of the evaporated vapor solution, allowing the formation of condensates. Exploiting the transparency of Si in the infrared (IR) spectrum, an IR camera monitors the condensation from above (Figure 1a).

In an attempt to demonstrate the versatility in EAD, we deposited various materials including (1) a lightly sulfonated graphene oxide dispersion (LSG); (2) graphene oxide with a NaCl additive (GO–NaCl); (3) GO at 0.5 and 0.1 wt %; and (4) lithium cobalt oxide (LiCoO2) purchased from MTI Corporation—with a variety of target deposition substrates including (1) Si wafers sonicated in ethanol (EtOH–Si); (2) Si wafers with 500 nm of thermally grown SiO2; (3) acrylic polymer substrates (the same on which the droplet is evaporating); (4) fused silica substrates coated with 80 nm of Al; and (5) Si wafers chemically etched with hydrofluoric acid (HF-etched Si). To test the applicability of the EAD method with other materials, additional EAD experiments were also conducted with organic droplet dispersions of MoS2. However, no additional data for MoS2 are provided because we did not successfully deposit MoS2 via the EAD method and these MoS2 samples were not aqueous dispersions like the other samples studied (see Figure 1c).

Figure 1c plots a scaled energy barrier for each key substrate–solution combination listed, where this energy barrier is calculated as the Laplace pressure multiplied by the free energy of the solid surface. The Laplace pressure scales with the sine of the equilibrium contact angle 

\[ \Delta P_{YL} \times \Delta G = \sin \theta_E \times (\cos \theta_a - \cos \theta_r) \]

and the free energy of a film covered by the solid substrate surface scales as 

\[ \Delta G \propto (\cos \theta_a - \cos \theta_r) \]

where \( \theta_E \), \( \theta_a \), and \( \theta_r \) correspond to the equilibrium, advancing, and receding contact angles, respectively. The scaled energy barrier, \( \Delta P_{YL} \times \Delta G \), is formulated by considering both a driving mechanism to cross the liquid–vapor interface (Laplace pressure component) and a substrate-capturing mechanism (free energy of a solid surface, \( \Delta G \)). Figure 1c reveals that the LSG/EtOH–Si (solution–substrate) combination has the lowest energy barrier.
ness, as expressed by the larger scaled energy barrier. Additionally, this scaled energy barrier estimation will pose issues when considering superhydrophobic surfaces (sin $\theta_k \rightarrow 0$). Correspondingly, the estimated energy barrier for the HF-etched Si ($\theta_k \approx 110^\circ$) provided in Figure 1c provides a lower estimate compared to the other substrates with $\theta_k \lesssim 90^\circ$.

Additional information on the nanomaterial dispersions/suspensions, substrates, and contact angle measurements is provided in the Supporting Information. It was initially presumed that application of additional external forces (e.g., electric or magnetic fields) can lower the energy barrier enough to achieve deposition with other nanomaterials which would otherwise have an energy barrier insurmountable with the setup.

Consequently, the formation of large condensates led to aggregation and the expected nonuniform capillary-induced condensation, irrespective of $\theta_k$. Additionally, no EAD deposits in superhydrophobic surfaces (sin $\theta_k \rightarrow 0$). An infuse rate of $\dot{m} = 9.8 \pm 0.6$ nL/s is also used to maintain steady-state evaporation at a constant volume. For all experiments, the droplet evaporation rate is held constant (i.e., keeping $R_e$, $\theta$, and $T_s$ fixed) and therefore condensation rates on the Si substrate are mainly dictated by the translational speed ($\bar{v}$) and separation distance ($\Delta z$) of the Si relative to the evaporating droplet dispersion (Figure 1b). Figure 2a–c shows the deposits of LSG by an EAD experiment conducted at slow translation speeds ($\bar{v} \approx 50 \mu m/s$) and small Si/droplet separations ($\Delta z \approx 150 \mu m$). The resulting high condensation rate (Figure 1c) led to significant droplet coalescence, forming droplets of up to ~15 nL. Rapid successive passes over the evaporating LSG droplet increase the amount transferred to the Si substrate (Figure 2b).

In an effort to produce uniform deposits, droplet coalescence can be regulated by decreasing the overall condensation rate. Yet, decreasing the overall condensation rate below ~100 pL/mm$^2$/s (measured using the image analysis method described in the Supporting Information) with the presented setup resulted in scarce deposits on the Si wafer. Additionally, no EAD deposits are detected when the Si substrate is heated to avoid condensation, irrespective of $\bar{v}$ and $\Delta z$; for example, no condensate is formed at Si wafer temperatures equal to or greater than the evaporating droplet temperature. This, in hindsight, is expected because just as there is an energy barrier for the GO to leave the evaporating droplet (i.e., cross the
liquid—vapor interface), there is also an energy barrier for the GO to deposit on the Si.

Raman spectroscopy has been reported as a quick technique for detecting graphene, with G-band and 2D-band peaks at $\sim 1580$ and $\sim 2700$ cm$^{-1}$, respectively. The Raman spectra for EAD-deposited LSG are provided in Figure 2c. The third peak at $\sim 1350$ cm$^{-1}$ (the D-band) arises for defected graphene (expected because of the oxygen and sulfonic acid functionalization). The relative intensity of the D-band varies slightly for each deposit, which is related to the defect density.

Null EAD experiments are performed (Figure 2d,e) to verify against false characterization of graphene caused by detecting the deposition of possible ambient hydrocarbons in the ambient air or aromatic compounds from the GO—sulfanilic acid synthesis. EAD performed with DI water shows no definitive Raman shift (Figure 2e), confirming that contaminants are not introduced from the ambient air environment. EAD with a null LSG solution (prepared by repeating the LSG synthesis without including GO) showed that residue deposits are visible via these “null” EAD sulfanilic acid depositions (Figure 2d). However, the Raman activity is weak (Figure 2e), and the peak positions ($\sim 1450$ and $\sim 2900–3000$ cm$^{-1}$) classify the deposits as an alkane. Thus, the main graphene peaks do not arise from any null experiments—confirming that LSG is deposited by the proposed EAD process.

Chemical functionalization of graphene introduces advances to various biological applications, though it tends to have low thermal stabilities. CVD and PVD (requiring high-temperature/high-vacuum environments) vaporize the material, removing chemical functionality, and therefore are not viable techniques for these technologies. The XPS spectrum (Figure 2f) confirms that the low-temperature ambient-pressure environment with EAD preserves the chemically modified graphene functionality. The carbon spectrum (Figure 2f(iii)) indicates asymmetry at higher binding energies due to the oxygen functionalization. The relative intensity of the functional groups is comparable to that of the LSG powder spectrum (Figure 2f(ii)). The lack of a strong C–O peak for GO is expected from the partial reduction of GO during the synthesis. Additionally, the sodium (Na) and sulfur (S) introduced during the preparation are present in both EAD-transferred LSG and powder (see the Supporting Information).

The vapor-phase transfer of solid LSG particles is a remarkable result. Although our proposed EAD transfer mechanism is still debatable, there is certainly an energy barrier that the particles must overcome to transfer across the liquid—vapor interface of the droplet. A theoretical investigation by Lima et al. shows that hydrophobic and hydrophilic surfaces develop double layers of opposite sign, providing an attractive force. Coupled with the mass transport due to evaporation, this ion-specific force between the hydrophilic (acrylic) and hydrophilic (Si) surfaces in our setup is hypothesized as possible contribution to the EAD transfer process. Although, additional forces are required for different solutions or target substrates, a relationship between the target substrate wettability and the contact angle hysteresis is used to determine the free energy for various solution—substrate setups (see the Supporting Information). As expected, the combination of LSG on Si has the lowest free energy (Figure 1c). The inability to deposit with the additional solutions—substrates is attributed to the larger free energy barrier. Additionally, a hydrophobic target substrate eliminates the additional attractive force, which may be influential in the transfer mechanism. From this, area-selective deposition is potentially viable with, for example, textured (or micro-/nanopatterned) hydrophobic/hydrophilic targets to facilitate favorable deposition in hydrophilic regions. Additionally, graphene, reported to have ferromagnetic features, may also be transferable by EAD in the presence of a magnetic field, although this was not systematically explored in this work.

To conclude, we present a material deposition technique utilizing a vapor-phase transfer of solid particles. By minimizing the liquid—solid free energy barrier with selection of a target substrate and fluid dispersion, we show that the mass transfer due to evaporation (among other possible forces such as an ion-specific attractive force) can exceed this energy barrier to transfer solid materials into the vapor phase. The additional energy barrier to deposit the material onto the target substrate against gravitational forces and replace the absorbed air molecules with GO is overcome by condensing the vapor. By avoiding the vaporization of the material (remaining as a solid), the material has also been shown to maintain its chemical functionality. Although we were not able to show that our proposed EAD technique is ubiquitous to all droplet dispersions of 2D materials, EAD still exhibits the potential for low-temperature deposition of 2D materials at atmospheric pressures.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01816.

Discussion of our laser etching methodology, condensation rate measurements, free energy calculations, fluid solution synthesis and characterization, and target substrate preparation and characterization using XPS (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

E-mail: shawn.putnam@ucf.edu (S.A.P.).

**ORCID**

Shawn A. Putnam: 0000-0002-9944-9466

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors thank Jean Calderon and Dr. Lei Zhai (University of Central Florida) for providing the GO solutions; Dr. Richard Vaia (Air Force Research Laboratory, Ohio) for providing the MoS$_2$ solutions; Dr. Nina Orlovskaya (University of Central Florida) for granting access to the Raman Spectrometer; and Dr. Sunil Kodambaka (University of California, Los Angeles) for insightful discussions.

### REFERENCES

1. Tsai, M.-L.; Su, S.-H.; Chang, J.-K.; Tsai, D.-S.; Chen, C.-H.; Wu, C.-I.; Li, L.-J.; Chen, L.-J.; He, J.-R. Monolayer MoS$_2$ heterojunction solar cells. ACS Nano 2014, 8, 8317–8322.

2. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-based composite materials. Nature 2006, 442, 282–286.

3. Perkins, F. K.; Friedman, A. L.; Coba, E.; Campbell, P. M.; Jernigan, G. G.; Jonker, B. T. Chemical vapor sensing with monolayer MoS$_2$. Nano Lett. 2013, 13, 668–673.
(4) Fowler, J. D.; Allen, M. J.; Tung, V. C.; Yang, Y.; Kaner, R. B.; Weiller, B. H. Practical chemical sensors from chemically derived graphene. ACS Nano 2009, 3, 301–306.

(5) Brittnell, L.; Gorbachev, R. V.; Jalil, R.; Belle, B. D.; Schedin, F.; Mishchenko, A.; Georgiou, T.; Katsnelson, M. I.; Eaves, L.; Morozov, S. V.; et al. Field-effect tunneling transistor based on vertical graphene heterostructures. Science 2012, 335, 947–950.

(6) Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High performance multilayer MoS2 transistors with scandium contacts. Nano Lett. 2013, 13, 100–105.

(7) Coleman, J. N.; Lotya, M.; O’Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; et al. Two-dimensional nanosheets produced by liquid exfoliation of layered materials. Science 2011, 331, 568–571.

(8) Liu, K.-K.; Zhang, W.; Lee, Y.-H.; Lin, Y.-C.; Chang, M.-T.; Su, C.-Y.; Chang, C.-S.; Li, H.; Shi, Y.; Zhang, H.; et al. Growth of large-area and highly crystalline MoS2 thin layers on insulating substrates. Nano Lett. 2012, 12, 1538–1544.

(9) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tománek, D.; Ye, P. D. Phosphorene: An unexplored 2D semiconductor with a high hole mobility. ACS Nano 2014, 8, 4033–4041.

(10) Hwang, W. S.; Remskar, M.; Yan, R.; Protasenko, V.; Tahy, K.; Chae, S. D.; Zhao, P.; Konar, A.; Xing, H.; Seabbaugh, A.; Jena, D. Transistors with chemically synthesized layered semiconductor WS2 exhibiting 105 S cm−1 room temperature modulation and ambipolar behavior. Appl. Phys. Lett. 2012, 101, 013107.

(11) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. Science 2004, 306, 666–669.

(12) Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun’ko, Y. K.; et al. High-yield production of graphene by liquid-phase exfoliation of graphite. Nat. Nanotechnol. 2008, 3, 563–568.

(13) Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. Nat. Nanotechnol. 2008, 3, 101–105.

(14) Stankovich, S.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. Carbon 2006, 44, 3342–3347.

(15) Wang, Y.; Li, Z.; Wang, J.; Li, J.; Lin, Y. Graphene and graphene oxide: Biofunctionalization and applications in biotechnology. Trends Biotechnol. 2011, 29, 205–212.

(16) Feng, Y.; Liu, H.; Luo, W.; Liu, E.; Zhao, N.; Yoshino, K.; Feng, W. Covalent functionalization of graphene by azobenzene with molecular hydrogen bonds for long-term solar thermal storage. Nanotechnol. 2006, 172.

(17) Jeon, H. G.; Huh, Y.; Yun, S. H.; Kim, K. W.; Lee, S. Y.; Lim, Y. S.; Yoon, D. H.; Lee, C.; Kim, J.-Y.; Ruoff, R. S. Unoxidized graphene/alumina nanocomposite: fracture- and wear-resistance effects of graphene on alumina matrix. Sci. Rep. 2014, 4, 5176.

(18) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman spectrum of graphene and graphene layers. Phys. Rev. Lett. 2006, 97, 187401.

(19) Pimenta, M. A.; Dresselhaus, G.; Dresselhaus, M. S.; Cançado, L. G.; Jorio, A.; Saito, R. Studying disorder in graphite-based systems by means of Raman spectroscopy. Phys. Chem. Chem. Phys. 2007, 9, 1276–1290.

(20) Lin-Vien, D.; Colthup, N.; Fateley, W.; Grasselli, J. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press, 1991.

(21) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Zhou, F.; McGinley, R. A. Raman spectrum of graphene and graphene layers. J. Phys. Soc. Jpn. 2014, 2, 2622.

(22) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Capillary flow as the cause of ring stains from dried liquid drops. Nature 1997, 389, 827–829.

(23) Lin, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; et al. Large-area synthesis of high quality and uniform graphene films on copper foils. Science 2009, 324, 1312–1314.

(24) Kim, K. S.; Zhao, Y.; Jiang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature 2009, 457, 706–710.

(25) Muratore, C.; Hu, J. J.; Wang, B.; Haque, M. A.; Bultman, J. E.; Jespersen, M. L.; Shammerberg, P. J.; McConney, M. E.; Naguy, R. D.; Voevodin, A. A. Continuous ultra-thin MoS2 films grown by low-temperature physical vapor deposition. Appl. Phys. Lett. 2014, 104, 261604.

(26) Marvin, L. F.; Roberts, M. A.; Fay, L. B. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry in clinical chemistry. Clin. Chim. Acta 2003, 377, 11–21.

(27) Lin-Vien, D.; Colthup, N.; Fateley, W.; Grasselli, J. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press, 1991.

(28) Jeong, H.-K.; Lee, Y. P.; Jin, M. H.; Lee, Y. H. Thermal stability of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon 2007, 45, 1558–1565.

(29) Jeong, H.-K.; Lee, Y. P.; Jin, M. H.; Lee, Y. H. Thermal stability of graphite oxide. Chem. Phys. Lett. 2009, 470, 255–258.

(30) Lima, E. R. A.; Bostrom, M.; Schwierz, N.; Sernelius, B. E.; Tavares, F. W. Attractive double-layer forces between neutral hydrophilic and neutral hydrophobic surfaces. Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys. 2011, 84, 061903.

(31) Ramakrishna Matte, H. S. S.; Subrahmanayam, K. S.; Rao, C. N. R. Novel magnetic properties of graphene: Presence of both ferromagnetic and antiferromagnetic features and other aspects. J. Phys. Chem. C 2009, 113, 9982–9985.