

Observation of Early to Full Covering Stages of Ethylene-based CVD of Graphene

K. Celebi*, J. W. Choi*, M. T. Cole**, A. O. Altun*, K. B. K. Teo***, H. G. Park*

* Institute of Energy Technology, ETH Zürich, Zürich CH-8092, Switzerland, parkh@ethz.ch

** Department of Electrical Engineering, University of Cambridge, Cambridge CB3 0FA, UK

*** Aixtron Ltd., Nanoinstruments, Buckingway Business Park, Anderson Road, Swavesey, Cambridge CB24 4FQ, UK

ABSTRACT

Scalable growth is essential for graphene-based applications. Recent development has enabled the achievement of the scalability by use of chemical vapor deposition (CVD) at 1000°C with copper as a catalyst and methane as a precursor gas. Here we report our observation of early stage of graphene growth based on an ethylene-based CVD method, capable of reducing the growth temperature to 770°C for monolayer graphene growth on copper. We track the early stages of slow growth under low ethylene flow rate and observe the graphene domain evolution by varying the temperature and growth time. Temperature-dependence of graphene domain density gives an apparent activation energy of 1.0 eV for nucleation.

Keywords: graphene, cvd, nucleation, ethylene

1 INTRODUCTION

Graphene is a two-dimensional monolayer of sp^2 -bonded carbon atoms, which has been attracting great scientific and technological interest since it was first discovered in the free-standing form.[1-2] Recent experiments on graphene have demonstrated important electrical phenomena such as huge electron mobility and ballistic transport,[1] existence of Dirac fermions [3-4] and room temperature quantum-hall effect; [5] as well as superior mechanical [6-8] and chemical properties. [9-10]

For scalable graphene growth, several synthesis methods have been reported. One way to obtain continuous graphene films is based on solutions that contain graphite oxide [11] or exfoliated graphene. [12-13] However, these chemical methods cannot fully recover the superior properties of a graphene monolayer. The epitaxial graphene growth by Si-desorption from single crystalline SiC surfaces [14-15] can result in a covering of larger areas. However, it does not only have high material and equipment costs, but also lacks a proper graphene transfer method. Recently, researchers have developed methods of chemical vapor deposition (CVD) to synthesize graphene on metal substrates. Initially these methods concentrated on the use of expensive single crystalline substrates of transition metals; [16] later the substrate costs have been reduced by the use of nickel [17-18] and copper [19] in CVD growth. Also, the use of

selective etchants can lead to easy transfer of the synthesized graphene on these cheaper metal surfaces. [17-20] While the costs and the transfer methods are similar for Ni and Cu, the proposed growth mechanisms are different. As Ni has a large solubility of carbon, a precipitation mechanism is responsible for the graphene growth on Ni, [17-18, 21] demanding fast cooling processes and hampering a fine control of the number of final graphene layers. For copper, on the other hand, it is the surface catalysis process that is believed to grow the graphene, prompting a great interest in this metal.

So far several groups have used methane (CH_4), as a carbon precursor for the surface catalysis process on copper. [19, 22-25] As shown in the CVD growth of CNTs, methane is a cleaner gas than other conventional carbon precursors, [26] but it requires higher temperatures compared to other precursor gases such as acetylene (C_2H_2) or ethylene (C_2H_4). Being more reactive and able to synthesize carbon nanomaterials at much lower temperatures, acetylene can easily lead to deposition of undesired amorphous carbon and degradation of the nanomaterial quality. [27] This degradation, however, can be controlled by the use of atomic hydrogen, which suppresses the decomposition of acetylene and ethylene [7, 26] and etches away the amorphous carbon deposits. [28] Although these two properties of hydrogen can improve the quality of the graphene, it can also have a detrimental effect of transforming the sp^2 bonds into sp^3 . [29] So, the hydrogen flow rate must be carefully chosen in using these carbon sources. An example of this graphene growth by CVD using acetylene has been demonstrated on copper films at a lower temperature, albeit with a large Raman D-mode intensity; [27] indicating the difficulty in controlling the amorphous carbon deposition by acetylene pyrolysis. However, compared to acetylene, ethylene has a lower reactivity, [30-31] promising an easier control for the lower temperature growth on Cu. While graphene production based on the ethylene precursor has been demonstrated by CVD on Ir(111) [16] and epitaxy on Ru(0001) [32] and crystalline Cu (111), [33] ethylene-based CVD of graphene has only recently been demonstrated on copper foils. [34]

Here we report our observation of early stages of graphene growth and characterization of graphene nucleation by *ex-situ* measurements of our ethylene-based short-time growths.

2 EXPERIMENTAL

All of our ethylene-based growths were carried out by use of a commercial CVD system (*Black Magic CVD System* by AIXTRON). As Cu substrates to grow graphene on, we employed Cu foils. (Alfa Aesar, 25 μm , 99.8% metals basis) For a typical process at 4.1 mbar, (Figure 1) native oxides on the Cu films/foils are reduced at 850°C (measured by infrared detector on the surface) using a 20-sccm flow of H₂, diluted by 1500-sccm of Ar for a duration of 30 minutes (including a 5-minute ramp of temperature from room temperature to 850°C). Reduction is followed by a 10-minute growth at the same temperature with an addition of 7 sccm of ethylene (C₂H₄) without altering the H₂ and Ar flows. The C₂H₄ flow is stopped immediately before the cooling step, to prevent precursor pyrolysis at lower temperatures. H₂ and Ar flows continue until the temperature reached 400°C and then the system further cools down below 100°C with the Ar flow only. The temperature, temperature ramp, pressure and flow rates were controlled by a software interface. A heated graphite stage provided the heating. We measured and controlled the sample substrate temperatures with an infrared temperature sensor.

For Raman characterizations, the graphene films are transferred onto SiO₂ by selective etch of the copper substrate. [18-19] Transferred films are characterized by micro Raman spectroscopy using a 532-nm laser at 2 mW with a focal spot size of ca. 0.4 μm . (WITec CRM 200) For characterizing surface morphology, we employed field emission scanning electron microscopy (Zeiss Gemini 1530 FEG) to image as-grown graphene films on copper foils.

3 RESULTS AND DISCUSSION

In order to be able to capture the partial covering by structurally simpler and smaller domains at the very early stages of the graphene growth, we used a low flow rate and

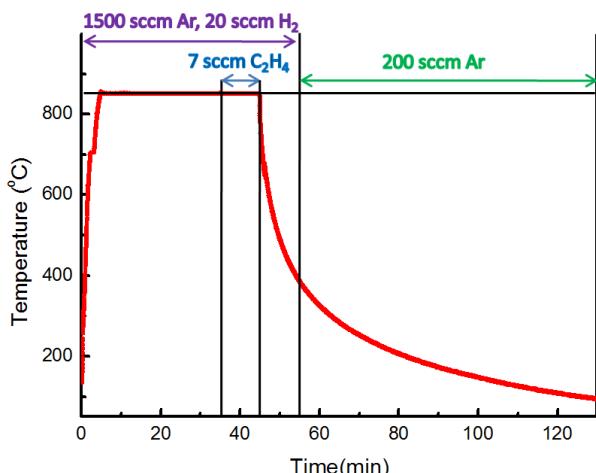


Figure 1: A typical CVD growth scheme, red curve shows the actual temperature measured by the infrared detector.

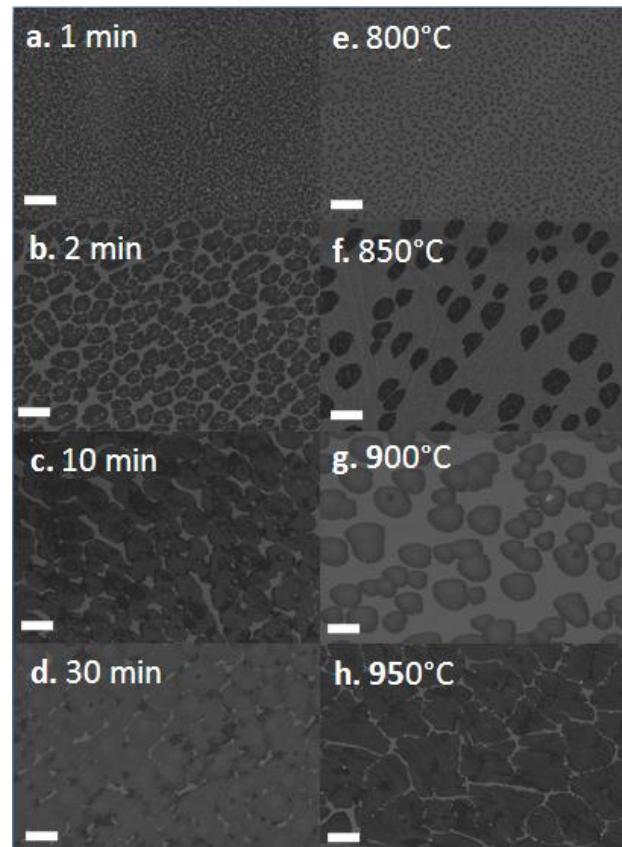


Figure 2: SEM images of the as-grown graphene on Cu foils. (a-d) Growth at 850°C for 1 min (a), 2 min (b), 10 min (c), 30 min (d). (e-h) Growth for 5 min at 800°C (e), 850°C (f), 900°C (g), 950°C (h). Dark regions correspond to the graphene domains. The size of the white scale bar is 2 μm .

partial pressure of ethylene and varied (1) the growth time while keeping the temperature at 850°C or the temperature while keeping the growth time at 5 minutes. We confirmed this partial graphene covering by small domains by taking the AFM (not shown here) and SEM images (Figure 3). We observe that the graphene domain size increases non-linearly by increasing the growth time from 1 minute to 30 minutes. We also see a similar trend of enlarged graphene domains by the growth temperature increasing from 800°C to 950°C, which is attributed to an increase in the graphene growth rate.

The Raman spectroscopy analysis bolsters quantitatively the SEM and AFM observations. Figure 3 shows the Raman spectra of the graphene films, grown at different temperatures, after being transferred to SiO₂ substrates. All spectra show three major peaks, being D, G and G' around 1350 cm^{-1} , 1590 cm^{-1} and 2690 cm^{-1} , respectively. These peaks can be fitted by single-Lorentzian functions. After the fitting, with the exception of the 800°C sample, the width of the G peaks lie in the range of 22-30 cm^{-1} and the width of the G' peaks lie between 40-45 cm^{-1} . These values suggest that our graphene is thin. [35] The samples with the

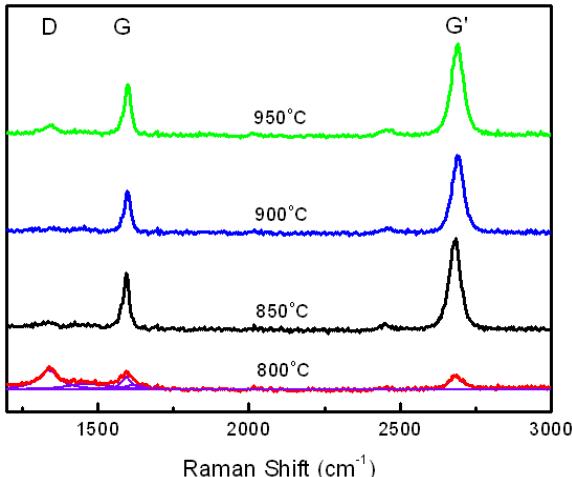


Figure 3: Raman spectra of as-grown graphene: growth temperature series. A 532-nm excitation was used.

small domain size show three additional disorder-oriented peaks, one at 1450 cm^{-1} , another at 1620 cm^{-1} (D'), and the other at 2900 cm^{-1} ($D+D'$). Due to these additional peaks, the Lorentzian-fitting must be done more carefully, as the D' peak is positioned near the G peak and can broaden it.

The characterization of graphene nucleation on copper was done by statistically counting the graphene domains per area on the SEM images. This number density decreases monotonically by increasing temperature, as reported before. [36] The corresponding Arrhenius plot for short time growths (just enough for nucleation) gives an apparent activation energy of 1.0 eV, while the deviation from linear trend at the highest temperature is due to a different regime of nucleation, both findings in line with previous reports for methane-based growths. [37]

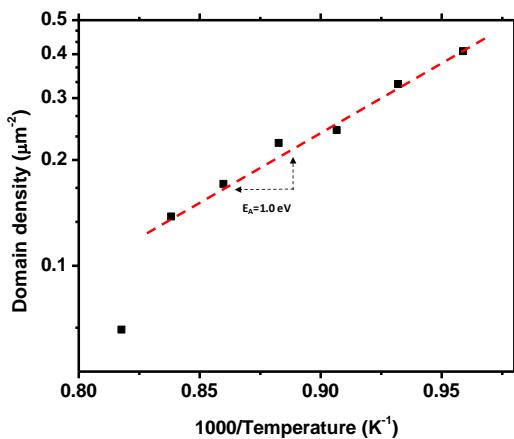


Figure 4: Arrhenius plot for the number density of graphene domains. Red line is the exponential fit.

4 CONCLUSIONS

We have demonstrated the use of the ethylene precursor in the CVD growth of graphene on copper films and foils. Our *ex-situ* observation of the partial covering of the copper surface by small graphene domains grown by short-time CVD runs at varied temperatures provides evidence of the lateral surface-catalyzed growth mechanism during the early stage of growth. Temperature has also been shown to increase the growth rate and decrease the final domain density. The apparent activation energy for graphene nucleation for our growth regime is 1.0 eV.

REFERENCES

- [1] K. S. Novoselov, *et al.*, "Electric Field Effect in Atomically Thin Carbon Films," *Science*, vol. 306, pp. 666-669, October 22, 2004 2004.
- [2] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat Mater*, vol. 6, pp. 183-191, 2007.
- [3] K. S. Novoselov, *et al.*, "Two-dimensional gas of massless Dirac fermions in graphene," *Nature*, vol. 438, pp. 197-200, 2005.
- [4] Y. Zhang, *et al.*, "Experimental observation of the quantum Hall effect and Berry's phase in graphene," *Nature*, vol. 438, pp. 201-204, 2005.
- [5] K. S. Novoselov, *et al.*, "Room-Temperature Quantum Hall Effect in Graphene," *Science*, vol. 315, pp. 1379-, March 9, 2007 2007.
- [6] C. Lee, *et al.*, "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene," *Science*, vol. 321, pp. 385-388, July 18, 2008 2008.
- [7] Y.-Q. Xu, *et al.*, "Effects of atomic hydrogen and active carbon species in 1 mm vertically aligned single-walled carbon nanotube growth," *Applied Physics Letters*, vol. 89, pp. 123116-3, 2006.
- [8] J. S. Bunch, *et al.*, "Electromechanical Resonators from Graphene Sheets," *Science*, vol. 315, pp. 490-493, January 26, 2007 2007.
- [9] D. C. Elias, *et al.*, "Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane," *Science*, vol. 323, pp. 610-613, January 30, 2009 2009.
- [10] X. Wang, *et al.*, "N-Doping of Graphene Through Electrothermal Reactions with Ammonia," *Science*, vol. 324, pp. 768-771, May 8, 2009 2009.
- [11] D. A. Dikin, *et al.*, "Preparation and characterization of graphene oxide paper," *Nature*, vol. 448, pp. 457-460, 2007.
- [12] Y. Hernandez, *et al.*, "High-yield production of graphene by liquid-phase exfoliation of graphite," *Nat Nano*, vol. 3, pp. 563-568, 2008.
- [13] V. C. Tung, *et al.*, "High-throughput solution processing of large-scale graphene," *Nat Nano*, vol. 4, pp. 25-29, 2009.

- [14] C. Berger, *et al.*, "Electronic Confinement and Coherence in Patterned Epitaxial Graphene," *Science*, vol. 312, pp. 1191-1196, May 26, 2006 2006.
- [15] K. V. Emtsev, *et al.*, "Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide," *Nat Mater*, vol. 8, pp. 203-207, 2009.
- [16] J. Coraux, *et al.*, "Growth of graphene on Ir (111)," *New Journal of Physics*, vol. 11, p. 023006, 2009.
- [17] K. S. Kim, *et al.*, "Large-scale pattern growth of graphene films for stretchable transparent electrodes," *Nature*, vol. 457, pp. 706-710, 2009.
- [18] A. Reina, *et al.*, "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition," *Nano Lett*, vol. 9, pp. 30-35, 2009.
- [19] X. Li, *et al.*, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils," *Science*, vol. 324, pp. 1312-1314, June 5, 2009 2009.
- [20] X. Li, *et al.*, "Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes," *Nano Letters*, vol. 9, pp. 4359-4363, 2009.
- [21] Q. Yu, *et al.*, "Graphene segregated on Ni surfaces and transferred to insulators," *Applied Physics Letters*, vol. 93, pp. 113103-3, 2008.
- [22] S. Bae, *et al.*, "Roll-to-roll production of 30-inch graphene films for transparent electrodes," *Nat Nano*, vol. 5, pp. 574-578, 2010.
- [23] A. Ismach, *et al.*, "Direct Chemical Vapor Deposition of Graphene on Dielectric Surfaces," *Nano Letters*, vol. 10, pp. 1542-1548, 2010.
- [24] M. P. Levendorf, *et al.*, "Transfer-Free Batch Fabrication of Single Layer Graphene Transistors," *Nano Letters*, vol. 9, pp. 4479-4483, 2009.
- [25] V. P. Verma, *et al.*, "Large-area graphene on polymer film for flexible and transparent anode in field emission device," *Applied Physics Letters*, vol. 96, pp. 203108-3, 2010.
- [26] M. Jung, *et al.*, "Growth of carbon nanotubes by chemical vapor deposition," *Diamond and Related Materials*, vol. 10, pp. 1235-1240, 2001.
- [27] Y.-H. Lee and J.-H. Lee, "Scalable growth of free-standing graphene wafers with copper(Cu) catalyst on SiO₂/Si substrate: Thermal conductivity of the wafers," *Applied Physics Letters*, vol. 96, pp. 083101-3, 2010.
- [28] A. Okita, *et al.*, "Effects of hydrogen on carbon nanotube formation in CH₄/H₂ plasmas," *Carbon*, vol. 45, pp. 1518-1526, 2007.
- [29] G. Zhang, *et al.*, "Ultra-high-yield growth of vertical single-walled carbon nanotubes: Hidden roles of hydrogen and oxygen," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 102, pp. 16141-16145, November 8, 2005 2005.
- [30] A. C. Ferrari, *et al.*, "Raman Spectrum of Graphene and Graphene Layers," *Physical Review Letters*, vol. 97, p. 187401, 2006.
- [31] X. Li, *et al.*, "Evolution of graphene growth on Cu and Ni studied by carbon isotope labeling," *Nano Lett*, vol. 9, pp. 4268-4272, 2009.
- [32] G. Nandamuri and et al., "Chemical vapor deposition of graphene films," *Nanotechnology*, vol. 21, p. 145604, 2010.
- [33] L. Gao, *et al.*, "Epitaxial Graphene on Cu(111)," *Nano Letters*, p. Article ASAP, 2010.
- [34] H. Shu-Jen, *et al.*, "Study of channel length scaling in large-scale graphene FETs," in *Symp. on VLSI Tech. (VLSIT)*, 2010, pp. 231-232.
- [35] L. M. Malard, *et al.*, "Raman spectroscopy in graphene," *Physics Reports*, vol. 473, pp. 51-87, 2009.
- [36] X. Li, *et al.*, "Large-Area Graphene Single Crystals Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper," *Journal of the American Chemical Society*, vol. 133, pp. 2816-2819, 2011.
- [37] H. Kim, *et al.*, "Activation Energy Paths for Graphene Nucleation and Growth on Cu," *ACS Nano*, 2012.