

OAK RIDGE NATIONAL LABORATORY
CENTER FOR NANOPHASE MATERIALS SCIENCES
Research Proposal

General Information

Proposal Number CNMS2020-A-00017	Proposal Type General
Title of Proposal Real-time characterization and control of graphene growth kinetics by pulsed CVD	
CNMS staff members contacted to discuss feasibility of project Geohegan, David B.	
State in your own words the reasons that led you to propose performing this research at the CNMS as opposed to some other facility, i.e., why are CNMS facilities or expertise needed? Tunable Raman system is required	

Participants

Name	Email Address	Institution	Role	On-Site
Smart, I. M.	im-smart@youruniv.edu	Your University	Principal Investigator	Y
Student, A. Grad	a.grad@youruniv.edu	Your University	Collaborator	Y
Colleague, Prof. A,	a.colleague@acoll.edu	Another College	Collaborator	Y
Fellow, Postgrad U.	post.fell@youruniv.edu	Your University	Collaborator	

CNMS Facilities Requested

Facility Group	Facility	Requested Usage
Electron & Atom Probe Microscopy	300kV aberration-corrected STEM/EELS (FEI Titan)	3 days
	Low-voltage (60-100kV) aberration-corrected STEM/EELS (Nion UltraSTEM)	3 days
	TEM Specimen Preparation (FIB, microtome, ion mill, etc.)	1 days
(LEAD) Functional Hybrid Nanomaterials	Laser Material Interactions and Processing with in situ diagnostics – heating, patterning, thinning, structuring, transfer, with XY scanning	5 days
	Optical Characterization and Laser Spectroscopy – ultrafast dynamics, microRaman, PL lifetime, UV-VIS-NIR, fluorometry, PLE	30 days
	Wet/Dry Assembly of Organic/Inorganic/Hybrid Films and Devices – dual glovebox evaporator, Sonospray, 2D stamping, perovskite PV	5 days
Scanning Probe Microscopy	Advanced SPM: air, liquid, glove box (cAFM, PFM, ESM, MFM, cKPFM, Raman)	5 days

Samples and Identification of Hazards

Research samples used in this project will be
 Synthesized at CNMS

Indicated hazards

No major safety issues

Categorization**Indicate any subjects that apply to this project**

Materials Sciences (including condensed matter physics, materials chemistry)

Funding**Source of Support**

DOE, Basic Energy Sciences

Funding Source

N/A

Funding Status

Funding has been obtained

Review Suggestions**List a few keywords to help in matching potential reviewers**

optical properties, graphene, CVD

Suggested reviewers from CNMS Review Committee

Rinzler, Andrew

Verduzco, Rafael

CNMS Review Committee members to exclude due to potential conflict of interest

Duscher, Gerd

Description of Proposed Research**1) What is/are the main scientific or technological question(s) that you plan to address?**

The unique thermal, electrical, and optical properties of graphene¹ may enable many potential applications involving this material, especially in the area of nanoelectronics². Among the many different methods of graphene synthesis, chemical vapor deposition (CVD) is the most attractive since it allows one to grow graphene on metal catalyst (e.g. Cu, Ni) patterned substrates.³ The majority of the recent studies are limited to simple empirical optimization of the CVD growth parameters. However, the growth mechanism of graphene is not very well-understood, thereby hindering the understanding required for potential applications and the major challenges are: (1) Control nucleation density and number of layers, (2) Rapid growth over large areas ("supergrowth?"), and (3) Growth of large, single-crystalline grains. An important question that is directly related to the discovery of new synthesis methods is whether graphene grows isothermally⁴, i.e., at the growth temperature, as it occurs in the case of catalyst-assisted carbon nanotube growth, or upon cooling^{5,6}? Surprisingly, the majority of published studies on Ni-CVD graphene growth are based on the premise that growth occurs during cool-down after deposition assuming dissolution precipitation mechanism, with no strong experimental evidence for such a view. Another question relates directly to the primary building blocks for graphene growth: does it grow from carbon atoms through the dissolution-precipitation mechanism, carbon clusters, or more complex intermediates through pure chemical assembly? Also, it is important to understand how fast graphene can be grown. Typically, it takes minutes to grow graphene on Ni and Cu. Can one grow graphene faster and what factors limit the growth rate? Considering that CVD growth of graphene is remarkably similar to that of carbon nanotubes - i.e., cap formation on a metal nanoparticle during the initial stages of nanotube growth is much like graphene growth on metal surfaces- our pulsed CVD approach (Fig.1a,b) developed for real-time studies of nanotube growth⁷⁻⁹ can be applied directly to monitor and control graphene growth. For example, mounting evidence from our in situ diagnostics studies of nanotube growth indicate that the initial stages of carbon nanotube growth include a flux dependent induction time⁸ (Fig. 1c), which can be described by autocatalytic kinetics, and begs the question: can the same kinetics describe the initial stages of graphene growth? Here we propose to perform UV-Raman spectroscopy at high temperatures at the CNMS in conjunction with our pulsed CVD approach to explore the role of feedstock flux in driving the growth kinetics of graphene.

2) Outline the overall technical approach that you plan to use to address the above questions. This section should provide the context for research tasks described below in sections (3), home institution activities, and (4), CNMS research.

To understand how graphene grows on “catalytic” metal films such as Ni - i.e., isothermally at the growth temperature or during cool down - and to explore its growth kinetics, we have proposed to combine pulsed CVD and several in situ optical diagnostics techniques, namely Raman scattering, direct optical imaging, and time-resolved reflectivity. Pulsed CVD approach will allow us to grow graphene incrementally, to limit the time available for nucleation and growth, and to measure transient nucleation and growth kinetics. In this proposal we'll focus on the use of in situ UV-confocal micro-Raman spectroscopy to explore the growth of graphene using well-defined pulses of hydrocarbon gas to understand growth mechanisms and kinetics.

3) What research tasks will be carried out at the users' home institution or elsewhere outside of the CNMS? Include any preliminary syntheses, measurements, or tests that have been/will be performed in preparation for the proposed research at the CNMS.

We'll provide a modified microscope Linkam stage (TS1500), which is capable to operate at low gas pressures required for this study.

4) Describe very clearly and specifically the research tasks to be carried out at the CNMS and the expected outcomes from the CNMS tasks. Include any technical milestones that must be met and the need for specialized capabilities and/or expertise at the CNMS for the research to be successful.

In this proposal we will focus mainly on the following two research tasks.

1. Feedstock flux dependence of graphene growth mode and kinetics.

To grow graphene we'll use a high temperature microscope stage (Linkam TS1500), which is modified to operate at low gas pressures. Some of the metal catalyst films will be deposited at CNMS using the Controlled Atmosphere Dual Glove Box Evaporator System. C₂H₂ gas pulses (ms-durations) will be ejected into the fast flow of Ar/H₂ through the microscope Linkam stage using a pulsed valve and graphene growth will be monitored in situ using Raman scattering. In the proposed experiments the Raman measurements will be conducted at high temperatures (700-900 C). Therefore, the black body radiation background is a big issue in these measurements. To minimize the blackbody radiation background in the Raman spectra during in situ monitoring of graphene growth at the elevated temperatures, we plan to use UV laser excitation (provided by Tunable Raman system at CNMS), which gives a small background. We expect that, similar to SWNT growth, both surface-growth and dissolution/precipitation can exist under certain circumstances. To determine if there is a clear crossover point or region, we will explore the feedstock flux dependence in selectively driving surface growth processes using pulsed CVD and in situ Raman scattering measurements. Using this approach we expect to find the conditions for fast surface driven growth of graphene and understand its growth kinetics at different growth regimes.

2. Kinetics of layer formation and evolution during graphene growth.

For some applications graphene with the specific number of layers is required. Therefore it is important to understand how the layers are forming during graphene growth. We propose to address this problem using in situ UV Raman scattering measurements through simultaneous detection of the G- and 2D-Raman bands. This real time measurements of the 2D/G ratio, which is directly related to the number of graphene layers (in the case of a few layer graphene) will allowed us to understand the mechanism and kinetics of graphene layer formation. Using this approach we'll be able to answer the questions if it is possible to control the number of layers using for example short pulses of a feedstock gas.

5) Provide an overall timeline for the CNMS tasks and describe how each facility/instrument that is checked on p. 2 will be used, including estimates of the number/quantities of samples, instrument time, CPU time, etc.

Each of the two tasks outlined above will require 15 days of the tunable Raman system time. The total required time is 30 days. In addition, approximately 10-15 samples should be analysed using SEM and 3-4 samples using aberration corrected microscopy at the ShaRE facility. To prepare graphene samples for TEM measurements we also will need laser processing facility to perform graphene cleaning after it transfer to a TEM grid.

6) What is your team's specific experience and expertise relevant to this research project?

Recently, we have developed methods to study the response of catalytically active surfaces to instantaneously changing source gas flux in a form of well defined pulses. The key feature of this pulsed CVD method is the use of real-time diagnostics based on time-resolved reflectivity (TRR) of a laser beam from the catalyst-coated substrate sampled at 200 Hz. Detailed computational models of the gas pulse evolution were developed to extract the kinetics of carbon nanostructure growth.[7-9] Here we propose to use similar approaches to understand the growth mechanisms of graphene.

Literature cited above

[1] Novoselov, K. S., Nobel Lecture: Graphene: Materials in the Flatland. Rev Mod Phys 2011, 83 (3), 837-849.

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[2] Rummeli, M. H.; Rocha, C. G.; Ortmann, F.; Ibrahim, I.; Sevincli, H.; Bornert, F.; Kunstmann, J.; Bachmatiuk, A.; Potschke, M.; Shiraishi, M.; Meyyappan, M.; Buchner, B.; Roche, S.; Cuniberti, G., Graphene: Piecing it Together. Adv Mater 2011, 23 (39), 4471-4490.

[3] Safron, N. S.; Kim, M.; Gopalan, P.; Arnold, M. S., Barrier-Guided Growth of Micro- and Nano-Structured Graphene. Adv Mater 2012, 24 (8), 1041-1045.

[4] Weatherup, R. S.; Bayer, B. C.; Blume, R.; Ducati, C.; Baehtz, C.; Schlogl, R.; Hofmann, S., In Situ Characterization of Alloy Catalysts for Low-Temperature Graphene Growth. Nano Lett. 2011, 11 (10), 4154-4160.

[5] Li, X. S.; Cai, W. W.; Colombo, L.; Ruoff, R. S., Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling. Nano Lett. 2009, 9 (12), 4268-4272.

[6] Reina, A.; Jia, X. T.; Ho, J.; Nezich, D.; Son, H. B.; Bulovic, V.; Dresselhaus, M. S.; Kong, J., Large Area, Few- Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. Nano Lett. 2009, 9 (1), 30-35.

[7] A. A. Puretzky, D. B. Geohegan, J. J. Jackson, S. Pannala, G. Eres, C. M. Rouleau, K. L. More, N. Thonnard, and J. D. Readle, Incremental growth of short SWNT arrays by pulsed chemical vapor deposition, Small (2012) published online DOI: 10.1002/sml.201102173.

[8] D. B. Geohegan, A. A. Puretzky, J. J. Jackson, C. M. Rouleau, G. Eres, and K. L. More, Flux-Dependent Growth Kinetics and Diameter Selectivity in Single-Wall Carbon Nanotube Arrays, ACS Nano 5 (10), 8311 (2011).

[9] J. J. Jackson, A. A. Puretzky, K. L. More, C. M. Rouleau, G. Eres, and D. B. Geohegan, Pulsed Growth of Vertically Aligned Nanotube Arrays with Variable Density, ACS Nano 4(12), 7573 (2010).

Publication record

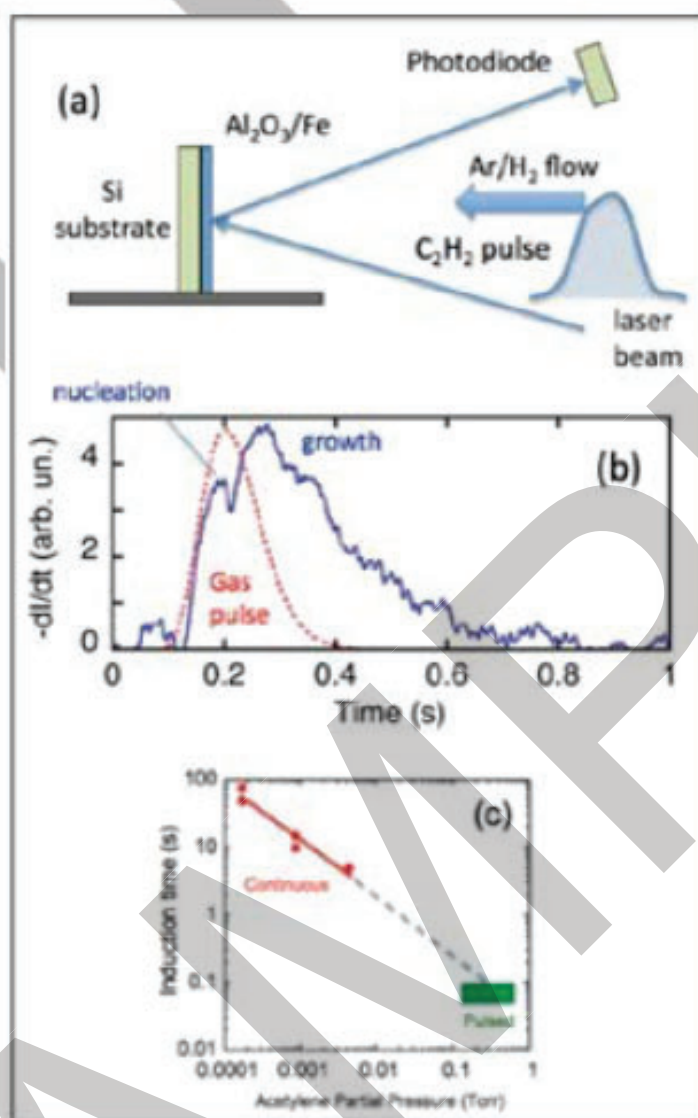


Fig. 1. (a) Pulsed CVD approach to probe nanotube growth kinetics. (b) Fast kinetics of SWNT nucleation and growth measured in situ. (c) C_2H_2 flux driven kinetics of SWNT growth [7-9]

Curriculum Vitae**Name of Principal Investigator:****Position Title:****Education/Training:****Institution and Location****Degree****Year(s)****Field of Study****Research and Professional Experience:****Professional Activities (last 5 years):****Significant Awards and Honors:**

Cumulative Total Number of Articles Published in Peer Reviewed Journals:

List Selected Peer Reviewed Publications Most Relevant to this Task (not to exceed 10):

Collaborators within the past 48 months: [e.g., R. Feynman (Cal Tech)]

Graduate and Postdoctoral Advisors:

Graduate Students and Postdoctoral Scholars Supervised: [e.g., J. London (Alaska State)]

A. Students:

B. Postdoctoral Scholars: