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Growth of Low-Dimensional Carbon Nanomaterials

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John Boeckl, Weijie Lu, William Mitchel, Howard Smith, Larry Grazulis, Gerry Landis, Said Elhamri, Kurt Eyink

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Outline

• AFRL Overview
• Low Dimensional carbon preview
• Atomic scale growth of Low-D carbon/SiC
• Growth of 3-D carbon nanostructures for potential thermal applications
• Summary
Outline

• AFRL Overview
  • Low Dimensional carbon preview
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AFRL Organization

AFRL Headquarters
Commander and Staff

AFOSR
Propulsion (RZ)
Directed Energy (RD)
Information (RI)
711 Human Performance Wing

Munitions (RW)
Sensors (RY)
Space Vehicles (RV)
Materials & Manufacturing (RX)
Air Vehicles (RB)
Human Effectiveness (RH)
Major AFRL Facilities

WRIGHT-PATTERSON
- PROPULSION (RZ)
- AIR VEHICLES (RB)
- SENSORS (RY)
- MATERIALS AND MANUFACTURING (RX)
- COLLABORATIVE C2 (RI)
- 711th HUMAN PERFORMANCE WING (HPW)
  - HUMAN EFFECTIVENESS (RH)

ROME
- INFORMATION (RI)
- SURVEILLANCE (RY)

HANSCOM
- BATTLE SPACE ENVIRONMENTS (RV)
- ELECTROMAGNETICS (RY)

EDWARDS
- ROCKET PROPULSION (RZ)

BALLSTON
- AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)

BROOKS
- 711th HPW
  - BIOEFFECTS (RH)
  - AEROSPACE PHYSIOLOGY (RH)
  - USAFSAM

TYNDALL
- AIR BASE TECHNOLOGY (RX)

KIRTLAND
- DIRECTED ENERGY (RD)
- SPACE VEHICLES (RV)

EGLIN
- MUNITIONS (RW)

Plus 40 Sites World-Wide

WSU Seminar – Feb. 2013
Accomplishing the RX Mission

- Revenue
- People
- Facilities & Equipment

LOCATIONS:
- Wright-Patterson AFB
- Tyndall AFB
- Program Offices in GA, OK, UT
- Collocates at TDs, SPOs, Centers
RX Demographics

PERSONNEL

DEGREES & SPECIALTY AREAS

388 Civilian/Military Scientist & Engineers (S&E)

- Materials Engineers
- Chemists/Chemical Engineers
- Research Physicists
- Aero Engineers
- Safety/Environmental Engineers
- Civil/Industrial Engineers
- Biologists/Microbiologists
- Mechanical Engineers
- Electrical Engineers

114 Contractors also have PhDs

Contractors (S&E, Technician, Ops Support)

On-Site 344 (MY Equivalent)
**Functional Materials Division**

**PRIMARY R&D FOCUS**

- Photonic Materials
- Soft Matter Materials
- Nanoelectronic Materials

**PRIMARY APPLICATION OUTLETS**

- Survivability
- ISR platforms
- Unconventional sensing
- Integrated power/energy
- Directed Energy

**CHALLENGES & OPPORTUNITIES**

- Laser/HPM hardening material solutions to ensure access to denied environments
- Improved material systems for continuous, robust, and non-conventional ISR applications
  - EO/IR, RF, and human system
- Facilitate improved human system and warfighter / machine interface
- Energy dense, compact / lightweight, autonomous power / energy AF-unique system applications
- Materials and components for near-zero collateral damage tactical strike and airborne self-defense
- Functional materials & processing motifs as integrated variables in component design
  - Non-traditional processing techniques enabling rapid, low-cost, custom devices
Nanoscale Transport Group

Develop and transition nanoscale engineered transport of electrons & phonons for C4ISR and EW components

**Impact:** Reduced energy consumption, improved capability, reliability and sustainability of C4ISR and EW systems

Material design for **enhanced electron and phonon transport**
- 2D-layers, nanowires, nanotubes, nanoparticles, etc.

Thin film processes with ICMSE optimization tools

Predictive modeling of material performance

Evaluation **in device prototypes**

Game changing materials and processes for above TRL3 maturation in **C4ISR and EW**

Requirements
System Eng.
Assessments

WSU Seminar – Feb. 2013
# Carbon Materials

## Research Team

### AFRL/RXPS:
- John Boeckl
- Bill Mitchell
- Kurt Eyink
- Shanee Pacley
- Dave Tomich
- Jeongho Park (Visiting Scientist)
- Shin Mou (NRC)

### AFRL/RXBT:
- Ajit Roy
- Adam Waite

### Contractors:
- University of Dayton Research Institute
  - Larry Grazulis
  - Said Elhamri
  - Gerry Landis
  - Howard Smith
- Wright State University
  - John Hoelscher
  - UTC
  - Weijie Lu

- OxyGon/Electron Microscopy
- Transport Measurements
- MBE, SE
- Raman
- X-ray
- MBE, XPS
- Transport/Device
- Modeling
- Thermal Measurements
- AFM, STM
- Transport Measurements
- Sample Preparation
- SIMS, XPS
- Raman
- Raman, XPS
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Low-D Carbon Basics

THE MOTHER OF ALL GRAPHITES

Graphene (below, top), a plane of carbon atoms that resembles chicken wire, is the basic building block of all the “graphitic” materials depicted below. Graphite (bottom row at left), the main component of pencil “lead,” is a crumbly substance that resembles a layer cake of weakly bonded graphene sheets. When graphene is wrapped into rounded forms, fullerenes result. They include honeycombed cylinders known as carbon nanotubes (bottom row at center) and soccer ball–shaped molecules called buckyballs (bottom row at right), as well as various shapes that combine the two forms.

Scientific American298(4), 68-75 (2008)
Potential Graphene/CNT Applications

Motivation

Material Properties

Ultra-high carrier mobility - $\mu \sim 10^4$ cm$^2$/V·s
High saturation velocity - $v = 10^8$ cm/s
High current carrying capacity – 1000x that of Cu
Excellent thermal conductivity - $\sim$5000 W/mK
Extreme strength - Young’s modulus $\sim$ 1.0 TPa
Flexible – Elastic modulus $\sim$ 0.25 TPa
Ultra-thin geometry – Single atomic layer

Application areas

• Digital electronics
• RF Electronics
• Flexible electronics
• THz/IR sources and detectors
• Spintronics at room temperature
• Thermal management for electronics
• Chemical sensors
Graphene Fabrication

1. Exfoliation from HOPG on SiO₂/Si wafers
2. CVD growth on substrates
3. Surface segregation on metal substrates
4. Epitaxial growth on SiC by Si sublimation

* Our Research Focus

Epitaxial Growth
1300°C - 1700°C
6√3 X 6√3 Surface reconstruction
Graphene is aligned with SiC crystal structure
Exfoliation – “The Tape Method”

• Discovered via exfoliation from graphite (circa 2004 – University of Manchester, UK)
• Simple method for research
• Generally creates small sheets on the order of hundreds of square microns

100 μm flake ~ $1000

Graphene Industries

Method is ideal for physics
Non-scalable & Cost prohibitive

PRL 97, 187401 (2006)
Graphene impact on nano-Science

- Graphene a new era of “Conductor Electronics”
- Band-gap created by interfaces, leading to possible new techniques toward bandgap engineering (substrate effects, nano-nano effects etc.)
- From 3D to 2D, new sciences and new knowledge are being created. 2D is used as a new approach in materials research even beyond carbon materials.
- Graphene has “multi-scale” structural integration from atomic scale to microns and beyond, which is an ideal nano-block materials for new 3D nano structures.
Challenges to Nanostructure Development

- The bridge between atomic design (chemistry synthesis, <1nm) and crystal growth (up to Inches) is not established.

- The general methods and principles for growth from atomic structures (chemistry) to nanostructures (1-100 nm) is not available. (only nanotechnology)

- Controllable assembly is not achieved, “materials by design” and “composites by design” have not been established.
  - Examples: chemical synthesis of graphene, controlled CNTs growth, high G dendrimer polymers, etc. are not yet fully successful.
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Graphene Preparation

- Commercial grade SiC wafer
  - 6H and 4H-SiC, Si-face (0001)
- Standard chemical clean
- Anneal in various chambers
  - Temperature: RT - 2100°C (TC, Pyrometer)
  - Pressure: Ar-ATM to 10^{-10} Torr
Growth of Graphene/SiC

**Growth in UHV**
@ 1200-1500˚C in Vacuum

**Growth in Ar ATM**
@ 1600-1700˚C in Ar ATM
1-30 min duration

SiC bilayer: 0.5nm
Current Growth Understanding

Mechanism based on surface morphology


Mechanism based on conversion of SiC lattice

The formation of one graphene layer requires about three SiC bilayers, and a transitional interface is formed when one or two SiC bilayers are decomposed.

All assuming SiC $\rightarrow$ Si (g) + C (s)


Quality vs Growth Conditions

- The quality of graphene grown in Ar is better than in vacuum.
- The quality of graphene grown in high vacuum $10^{-4-5}$ torr is better than in ultra-high vacuum ($<10^{-8}$ torr).

*High purity Ar contains 0.1-1 ppm oxygen, about $10^{-3-4}$ torr oxygen in 1 atm Ar*

The available models cannot explain why oxygen helps the growth of graphene?
Oxygen Impact on Growth

1450°C in UHV chamber for 30min (oxygen was not detected)  
O₂<10⁻¹⁴ torr

1450°C in UHV chamber for 30 min (with oxygen leak valve)  
O₂ @ 8 x10⁻¹¹ torr
Oxygen Effect on SiC surface

Annealed at 1400°C, at 10⁻⁸ torr (UHV) for 30min

Preheated at 700°C in oxygen at 10⁻³ Torr for 5 min, cooled and then heated to 1400°C for 30 mins at 10⁻⁸ torr (UHV)
Surface Chemistry with Oxygen

\[
\begin{align*}
\text{SiC (s) + } & \frac{1}{2} \text{O}_2 (g) \rightarrow \text{SiO (g) + C (s)} & \text{Eq. 1} \\
\frac{1}{2} \text{SiC (s) + } & \frac{1}{2} \text{CO (g) } \rightarrow \frac{1}{2} \text{SiO (g) + C (s)} & \text{Eq. 2} \\
\text{SiC (s) + H}_2\text{O (g) } \rightarrow & \text{SiO (g) + C (s) + H}_2 (g) & \text{Eq. 3} \\
\text{SiC (s) + CO}_2 (g) \rightarrow & \text{SiO (g) + CO (g) + C (s)} & \text{Eq. 4} \\
\text{SiC (s) } \rightarrow & \text{Si (g) + C (s)} & \text{Eq. 5}
\end{align*}
\]

- Preferential sublimation of Si from SiC surface and subsequent conversion of free carbon to graphene or CNTs
- Structure of the interface? Nature of chemical bonding?
- Transition from SiC to graphene
- Mechanism of the growth process?
Mechanism Based on Interface Chemical Reactions

Graphene growth process on SiC via a defective surface layer

- An interface transition layer a few nm thick is formed above 1100°C
- The structures of this interface layer is unknown
- The interface layer decomposes at a lower temperature than SiC

SiC (s) + O₂ (g) → SiCₓOᵧ (s) → SiO (g) + C (s)

“Surface compositional analysis of graphene/SiC (0001)”,
R. L. Barbosa, et.al., submitted to ICSCRM 2011
1100°C To form an interface layer

The layer decomposes at 1400°C

1600°C

Atomic Growth Model
1. A carbon rich layer on the SiC surface is formed at high temperature
2. The interaction of the residual oxygen with carbon forms thermally stable oxygen-carbon embedded structures.
3. Depending on environment such structures lead to curvature of hexagonal structures resulting in the formation of CNT nanocaps or planar graphene

Interface transition layer before/after graphene formation
X-Ray Photoelectron Spectroscopy

Sample Composition
- SiC
- Graphene (C-C $sp^2$)
- $\text{SiO}_x \text{C}_y$
  - C 1s $sp^3$
  - Si 2p $\text{SiO}_x \text{C}_y$
  - O 1s C-O
- *O-C (Bulk component)
Role of Oxygen in SiC Decomposition

The Key Issue to produce carbon on SiC
The reaction must be controlled in active oxidation, not forming SiO₂

Region 1: Active oxidation, Si(g)/SiO(g)

\[ \text{SiC(s)} + \frac{1}{2} \text{O}_2(g) = \text{SiO(g)} + \text{C(s)} \]
\[ \text{SiC(s)} = \text{Si(g)} + \text{C(s)} \]

Region 2: Active oxidation, SiO(g)

\[ \text{SiC(s)} + \text{O}_2(g) = \text{SiO(g)} + \text{CO(g)} \]

Region 3: Passive oxidation, high O₂, SiO₂(s)

\[ \text{SiC(s)} + \frac{3}{2} \text{O}_2(g) = \text{SiO}_2(s) + \text{CO(g)} \]

Growth by Interface Decomposition


Thermally stable O-C compounds

Goal to understand the thermal stable O-C compounds by TEM, TPD, and modeling

Thermal desorption spectra of CO (a) and CO₂ (b) after oxygen implantation for various carbon materials. (EK98: pure graphite, and USB15: 15% B in C),

Temperature region for CNT and graphene growth


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Graphene Growth Conclusions

• Graphene is formed above ~1400°C
• Oxygen may play a role in the initial growth of graphene on SiC
• XPS shows oxy-carbides, $sp^3$ and $sp^2$ carbon structures
• Proposed growth model with oxygen
  $SiC \ (s) + O_2 \ (g) \rightarrow SiC_{x}O_{y} \ (s) \rightarrow SiO \ (g) + C \ (s)$
• The controlling steps:
  $SiC \rightarrow SiO_xC_y \rightarrow SiO + C \rightarrow C \ sp^3 \rightarrow C \ sp^2$
## Literature evidence for large variation of growth temperature (~ 300°C)

<table>
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<th>H-etch</th>
<th>T(√3 x √3) (°C)</th>
<th>T(6√3 x 6√3) (°C)</th>
<th>Graphene growth (°C)</th>
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<tr>
<td>Luxmi et al. [54]</td>
<td>Yes</td>
<td>NR</td>
<td>1150</td>
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<td>Starke and Riedl [15]</td>
<td>Yes</td>
<td>950</td>
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<td>Jernigan et al. [55]</td>
<td>Yes</td>
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<td>Van Bommel et al. [56]</td>
<td>No</td>
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<td>Rollings et al. [20]</td>
<td>No</td>
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<td>Riedl et al. [16]</td>
<td>Yes</td>
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<tr>
<td>Huang et al. [19]</td>
<td>No</td>
<td>NR</td>
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<tr>
<td>Charrier et al. [15]</td>
<td>No</td>
<td>NR</td>
<td>&lt;1080</td>
<td>1200</td>
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<tr>
<td>Seyller et al. [21]</td>
<td>No</td>
<td>1050</td>
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<td>1400</td>
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<tr>
<td>Aoki et al. [57]</td>
<td>No</td>
<td>1100</td>
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<td>1550</td>
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<tr>
<td>Berger et al. [58]</td>
<td>Yes</td>
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<td>Park et al. [59]</td>
<td>No</td>
<td>1050</td>
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<tr>
<td>Chen et al. [17]</td>
<td>No</td>
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<tr>
<td>Johansson et al. [60]</td>
<td>No</td>
<td>900</td>
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<td>Hannon et al. [61]</td>
<td>No</td>
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<td>Forbeaux et al. [13]</td>
<td>No</td>
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Low-D Carbon Nanostructures on SiC

**Growth of graphene/SiC**
- Growth at 1200-1500°C in UHV, or at 1600-1800°C in Ar for 1-30 min

**Growth of SWNTs/SiC structure**
- Growth in high vacuum at 10^{-6} to 10^{-7} torr ~1400°C

**Growth of MWNTs/SiC structure**
- Growth in high vacuum at 10^{-3} to 10^{-5} torr at 1400-1700°C up to 2 um long

**Standard growth conditions and results**
- Annealing from 1400-1700°C
- Vacuum from 10^{-2} to 10^{-10} torr
- Products: SWNTs, MWNTs and graphene.
- No amorphous carbon and no Si in the products
- Metal-free and well aligned structures

An ideal space for studying mechanism/kinetics of Low-D materials
Growth Parameter: Pressure

- **UHV** - (10^{-8} to 10^{-10} Torr) Graphene
  - LEEM, LEED, XPEEM, MBE studies
  - Graphene formation

- **HV** - (10^{-5} to 10^{-7} Torr) Low CNT growth rate
  - Turbo pump on

- **LV** - (10^{-2} to 10^{-4} Torr) High CNT growth rate

- **LLV** - (<10^{-2} Torr) No growth, burning?

- **ATM** – (Argon background) graphene
• **Oxygen as a gas phase graphitization catalyst**

Oxygen in the range of 2 to 20 torr accelerates the graphitization process. Ar and N² have no effect on graphitization. Oxygen atoms may remove the amorphous carbon atoms by chemical reaction, “Effect of gas phase on graphitization of carbon”, T. Noda, and M. Inagaki, Carbon, 2, 127 (1964).

• **Metal catalytic CNT synthesis involving oxygen**

2. Rümmeli et al. have suggested a mechanism of oxygen assisted SWNTs metal catalytic growth, i.e., nucleation via oxygen etching carbon shells. Nano-Lett. 5, 1209 (2005).
3. Dai et al suggested that oxygen controls the C/H ratio and provides a C-rich condition in favor of CNT formation, PNAS, 102, 16141 (2005).

• **Oxides as catalysts in CNTs synthesis**

Liu et al., Importance of Oxygen in the Metal-Free Catalytic Growth of Single-Walled Carbon Nanotubes from SiOx by a Vapor-Solid-Solid Mechanism”, JACS, 2011
Metal-free SWNTs on SiC

- Si-face SiC, at 1400°C, 10^{-6-7} Torr
- Radial breathing mode centered at 191 cm^{-1}
- Diameter of SWNT is 1.3 nm

Other diameters demonstrated by:
Metal-free MWNTs on SiC

- Metal-free CNTs
- Well-aligned on SiC
- Low structural defects

Oxygen is at $10^{-8}$ torr when the total pressure is at $10^{-5}$ torr
Carbon on SiC: Summary

- Complex growth process
  - Difficult environment for in-situ tools
  - Use modeling to assist in understanding
- We predict oxygen plays critical role in controlling growth
  - Need to know residual gas levels in system
  - Can be used for preferential structure growth
  - Evaluating model to study molecular oxygen adsorption
- Graphene
  - Layer control reasonable
  - Electronic quality improvements still needed
- CNT’s
  - Structurally attached to the SiC substrate
  - Vertically aligned to SiC substrate
  - Non-metal catalyst method
Pillared Carbon Architecture

- Bottom-up approach: 3-D Pillared Architecture
- Thermal transport limited by CNT-graphene junction
- Variations by changing CNTs density and distance between graphene layers
- Growth based on theory of oxygen atomic catalysis for Low-D carbon

Pillared Carbon Structures on SiC

• Pillared graphene-CNTs on SiC can be produced
• Great for modeling
• Excellent structures for investigating thermal nano-science

Goal
To control the growth of low-dimensional carbon nanostructures enabling application specific materials to be produced.
Preliminary Conclusions

**Approach**

- Evaluate the atomic structures by TEM, SEM, Raman, and IR
- Understand the structures of CNTs-graphene junctions and correlate with phonon properties

**Result**

- The first group to grow Pillared graphene structures at the atomic scale
- A new high performance thermal material with promising applications in high power electronics

---

**Heated from bottom**

**Pillars of CNT/graphene stacks**

**IR microscopy (x12)**

120°C on the substrate (unpublished data)
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Conclusions

- Focus on chemistry and atomic catalysis for growth from atomic to nano scale and beyond
- A preliminary atomic oxygen catalytic growth mechanism for low-D carbon nano-structure growth
- Experimental data has shown that the proposed mechanism could be applied to growth of pillared graphene architectures