Synthesis and Characterization: Low-Dimensional Carbon Nanomaterials on 3C-SiC/Si

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Synthesis and Characterization: Low-Dimensional Carbon Nanomaterials on 3C-SiC/Si

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Outline

• Background on Low-D Carbon Materials
  • Graphene Synthesis on Bulk SiC
• 3C-SiC on Si
  • Epitaxial Growth
  • Synthesis of Graphene
• Future Direction
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• Background on Low-D Carbon Materials
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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.

Graphene/CNT Properties

Material Properties

- Ultra-high carrier mobility - $\mu \sim 10^4 \text{ cm}^2/\text{V} \cdot \text{s}$
- High saturation velocity - $v = 10^8 \text{ cm/s}$
- High current carrying capacity - 1000x that of Cu
- Excellent thermal conductivity - $\sim 5000 \text{ W/mK}$
- Extreme strength - Young's modulus $\sim 1.0 \text{ TPa}$
- Flexible - Elastic modulus $\sim 0.25 \text{ TPa}$
- Ultra-thin geometry - 1D Tube or 2D atomic layer

Graphene Fast Facts

- Three million sheets of graphene on top of each other would be 1mm thick
- Graphene is the most impermeable material, even helium atoms cannot squeeze through
- Graphene is incredibly transparent, yet, you can still see this single layer of atoms with your naked eye
Key Materials Challenges: Graphene

- **Large scale production of high-quality graphene**
  - Doping the material
  - Ribbon processing
  - Edge control

- **Need for a band gap**
  - Functionalizing
  - Interfaces/Interconnects/Contamination

- **Single surface of atoms**
  - Beyond graphene
  - MoS$_2$, WS$_2$, hBN, etc....
  - Gate Dielectrics
  - Heterostructures

**2-D material development**

Impact of Materials on Society

Wide-ranging Applications

Incredible Possibilities
Like plastic, graphene has the potential to be used in a vast variety of materials and situations

**Computing**
- All carbon electronics and computer chips
- Smaller, faster, lower power, electronics
- Flexible electronics
- No need for cooling

**Structural**
- Additive to plastics for smaller lighter composites
- Laminates with improved strength
- Transportation vehicles become lighter and stronger improving efficiency and safety

**Energy and Optics**
- Longer life batteries and better solar cells that are flexible, cheap and mass producible
- Flexible touch screens, LCDs and LEDs
- Brighter, lower voltage, and higher current robust field emitters
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
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 Parameter: Pressure

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

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

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

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

- **ATM** – (Argon background) graphene
Graphene Quality

Graphene starts to form at 1700°C with highest mobility grown in the vicinity of 1700-1750°C under vacuum.
Surface Chemistry w/Oxygen

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

- 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?
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

\[
\text{SiC (s) + O}_2 (g) \rightarrow \text{SiC}_x\text{O}_y (s) \rightarrow \text{SiO (g)} + \text{C (s)}
\]

“Surface compositional analysis of graphene/SiC (0001)”,
R. L. Barbosa, et.al., ICSCRM Proc. 2011
Partially Disordered Interface

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

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

ICMSE Applied to Defect Engineering in Low-dimensional Compounds

**Objective:** Integrate calculation of properties with in-situ experiments for tightly coupled iterative validation and understanding of materials behavior (Raman signatures, formation energies, ground state structures.)

**Experimental**

- **ARES Schematic** (Adaptive Rapid Experimentation & in-situ Spectroscopy)
  - Laser: 532 nm
  - Growth Conditions:
    - Chamber pressure: 10^{-6} Torr
    - Laser power: 2.5 W
    - Excitation time: 60 min
  - Vacuum Chamber
  - SiC Wafer:
    - Grow nanostructures via thermal decomposition of SiC
    - Collect Raman spectra in-situ
    - Obtain growth kinetics
  - Gases In
  - NV2 Translation
  - Vacuum

- **Modeling Defects in Graphene**
  - Reconstruction via atom elimination/bond rotation
  - Oxygen adsorbed on graphene

- **Reconstruction via atom elimination/bond rotation**

- **Experimental**

- **Oxygen adsorbed on graphene**


Graphene on Bulk SiC Conclusions

- Graphene is formed above \(~1400^\circ\text{C}\)
- 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
  \[
  \text{SiC (s) + O}_2 (g) \rightarrow \text{SiC}_{x}\text{O}_y (s) \rightarrow \text{SiO (g)} + \text{C (s)}
  \]
- The controlling steps:
  
  \[
  \text{SiC} \rightarrow \text{SiO}_{x}\text{C}_y \rightarrow \text{SiO} + \text{C} \rightarrow \text{C} \quad sp^3 \rightarrow \text{C} \quad sp^2
  \]
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Why graphene on SiC/Si?

~Holy Grail!
Enables minimum effort wafer-scale devices:

- Reduced Cost
- Transfer–Free
- Flexible membranes
- Self–aligned patterning
- Combination of 2 outstanding materials
- Exploit existing graphene synthesis
3C-SiC on Si at Griffith University

Epitaxial SiC on Silicon: core expertise

June 2013: ANFF launch @ Griffith of the 300mm epitaxial reactor

LPCVD reactor
Large area
3C-SiC epitaxial sequence

Alternating-Supply/Atomic-Layer Epitaxy (ASE/ALE)

Surface clean

SiC

Carbonization

SiC

Epitaxial growth

Stacking faults in 3C-SiC

SiC(111) more defective than SiC(100): different relaxation kinetics
Quality of the 3C-SiC Films

As-deposited thin films (<100nm)

The as-grown thin SiC films are yet fully crystallized with predominant stacking fault throughout the film thicknesses.

As-deposited thick films (>400nm)

Single crystalline 3C-SiC is observed and the film quality improves as thickness increases.

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  • Metal Catalyst (not reported in this talk)
  • Thermal Decomposition (UHV/Anneal Furnace)
Sublimation from SiC/Si

B. Gupta et al, Carbon, 2014

Ultra High Vacuum $P \approx 5 \times 10^{-11}$ Torr, $1300^\circ$C, in situ STM
Sublimation from SiC/Si

Need for $T > 1300^\circ C$ to obtain acceptable quality *epitaxial graphene*

UHV system low residual gas
Oxygen effect in low vacuum furnace?
Experimental Aspects
Decomposition to Graphene

- Argon or Vacuum (10^{-5} torr)
- 1100-1350°C (on 3C-SiC)
- 50mins - 3hours
- ramp-up rates (3-20°C/min)
- cooling rate (5-6°C/min)

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>“3C-SiC”</td>
<td>Si (100)</td>
<td>6 nm</td>
</tr>
<tr>
<td>“3C-SiC”</td>
<td>Si (100)</td>
<td>90 nm</td>
</tr>
<tr>
<td>“3C-SiC”</td>
<td>Si (111)</td>
<td>6 nm</td>
</tr>
<tr>
<td>“3C-SiC”</td>
<td>Si (111)</td>
<td>93 nm</td>
</tr>
</tbody>
</table>
Graphene starts to form at 1150°C after prolonged time with better quality at 1200°C for 1h under vacuum. In-situ SiC crystallization occurs, and longer heating time result in the formation of 6H-SiC.

"3C-SiC on Si substrates"
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Future Direction

Pillars for Rapid Growth Experimentation

Future Direction
Pillars for Rapid Growth Experimentation

1. Improved etch at Griffith
2. Use SOI to improve thermal isolation

3C-SiC on Si: Bulk and surface Si micromachining!
## Future Direction

**Self-aligned Sublimation**

<table>
<thead>
<tr>
<th>Process</th>
<th>Diagram Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epitaxial SiC on Si(111)</td>
<td>Epi SiC, Silicon</td>
</tr>
<tr>
<td>Photolithography</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiC plasma etching</td>
<td>Silicon</td>
</tr>
<tr>
<td>Photoresist strip</td>
<td>Silicon</td>
</tr>
<tr>
<td>Release of the microbeams</td>
<td>Silicon</td>
</tr>
<tr>
<td>Self-aligned graphene by sublimation</td>
<td>Silicon</td>
</tr>
</tbody>
</table>
For the first time, stress gradients measured with ~10nm resolution bring new insights...

Future Direction
Membrane Etch into Higher Quality Epi-layer

Future Direction
Membrane Etch into Higher Quality Epi-layer

Graphene
3C-SiC
Si

20nm

50 nm
Future Direction

Membrane Etch into Higher Quality Epi-layer

Graphene

3C-SiC

Si

20nm

50 nm
Carbon Research Group

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Raman, XPS, Growth
MBE, XPS
Modeling
AFM, STM
Sample Preparation
SIMS, XPS
Transport Measurements

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