Large Area Plasma-Enhanced Chemical Vapor Deposition of Nanocrystalline Graphite on Insulator for Electronic Device Application

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Outline

• Why PECVD for graphene deposition?
• PECVD system and deposition
• Nanocrystalline graphite (NCG)
• Device fabrication
• Conclusion
Why PECVD for graphene growth?

Comparison of methods for growth of graphene

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<tr>
<th>Method</th>
<th>Advantage</th>
<th>Disadvantage</th>
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<tr>
<td>Exfoliation from graphite</td>
<td>Highest quality</td>
<td>Random (shape, size, location)</td>
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<tr>
<td>Epitaxial growth on SiC</td>
<td>Good Control over number of layers</td>
<td>Expensive substrates</td>
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<td>Large domains</td>
<td>High temperature</td>
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<td></td>
<td></td>
<td>Surface steps</td>
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<tr>
<td>Catalytic growth on metal</td>
<td>No limit of substrate size</td>
<td>Requires graphene transfer for electronic application</td>
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- Research into growth methods not exhausted
PECVD deposition

- PECVD in use for large-area uniform film deposition
- Different plasma-enhanced CVD methods for graphene or graphene-like film deposition reported
  - Remote PECVD [1]
    → Custom built/modified equipment
  - Surface wave PECVD [2]
    → On metal, requires transfer
- Evaluate the PECVD route further

Chemistry and PECVD System

- Carbon source \((\text{CH}_4) \rightarrow \text{CH}_x, \text{C}_2\text{H}_y, \text{C}_3\text{H}_z, \text{H}\)
- Chemical binding followed by hydrogen desorption
- PECVD system used
  - Oxford Instruments Nanofab 1000 Agile
  - 200 mm substrates, parallel plate configuration

www.oxford-instruments.com
• Si wafer with 240 nm thermal oxide
1. Heat-up from loading to processing temperature
2. Hydrogen pre-treatment
3. PECVD deposition
4. Cool-down and unload

(step durations are typical values)
Deposition uniformity

- 15 minutes, 900°C, 100 W RF, 90 sccm H₂, 72 sccm CH₄ → 30-37 nm thickness

150 mm (6”) substrate

Ellipsometer thickness mapping

\[ \text{Max} - \text{Min} = \frac{\text{Max} - \text{Min}}{\text{Max} + \text{Min}} \times 100\% \]
• Deposited films exhibit distinct D (1350 cm\(^{-1}\)), G (1600 cm\(^{-1}\)) and broad 2D (2700 cm\(^{-1}\)) peaks
• \(I(D)/I(G) = 2.06\)
• Film described before [3]
  1. G-peak position unaffected by \(\lambda\) (1600 cm\(^{-1}\))
  2. \(I(D)/I(G) \approx 2\)

→ Nanocrystalline graphite

• NCG is a film with crystalline ("graphene") domains in random orientation

• Size of crystalline domains $L_a$ can be estimated from $I(D)/I(G)$ ratio [4]

\[
\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a}
\]

• Our films

$L_a = 2.2$ to $2.7$ nm

Other deposition conditions

![Graph showing Raman shift vs. intensity for different deposition conditions.

- 750°C, 5 nm: 532 nm peak at 1350 cm⁻¹ for D, 1600 cm⁻¹ for G, and 2700 cm⁻¹ for 2D.
- 800°C, 9 nm: Similar peaks as above, but at slightly different positions.
- 850°C, 9 nm: Additional peaks at 1300 cm⁻¹ for D and 1500 cm⁻¹ for G.
- 900°C, 2.5 nm: Peaks at 1350 cm⁻¹ for D, 1600 cm⁻¹ for G, and 2700 cm⁻¹ for 2D.
- 900°C, 13 nm: Additional peaks at 1250 cm⁻¹ for D and 1450 cm⁻¹ for G.
- 900°C, 30 nm: Peaks at 1350 cm⁻¹ for D, 1600 cm⁻¹ for G, and 2700 cm⁻¹ for 2D.

Raman map:

- NCG Thickness in nm vs. Position:
  - 17%: 8% variation.
  - 19%: 9% variation.

- Color scale ranges from 2.0 to 2.3 for (ID)/(IG).
Device fabrication

- Contacted NCG strips fabricated

1. Thermally oxidized substrate with NCG film
2. Lithography
3. Oxygen-based dry etch of NCG and resist strip
4. Ti/Au contact patterning by lift-off

NCG

SiO₂

Ti/Au

nano-crystalline graphite

SiO₂

10 μm

Ti/Au pad
• Fabricated devices
$\rho = 0.029 \, \Omega \, \text{cm}$

• Van der Pauw
$\rho = 0.012 \, \Omega \, \text{cm}$

$R_{\text{contact}} = 1.38 \, \text{k}\Omega$
Film transparency

- NCG deposited on quartz and sapphire
- Optical transmission measured

- 85% transparency @ 13 kΩ/sq for 6 nm film on quartz glass
Conclusion

- Demonstrated large-area, meta-free PECVD of nanocrystalline graphite
- Uniform NCG coverage over 150 mm substrates
- Substrate size not limited
- Sheet resistance in kΩ/sq range
- NCG optical transparency > 85%
- NCG can be easily patterned and contacted
- Potentially usable for transparent electrodes
### Growth comparison

**Lets look at the comparison again**

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<td>Use adhesive tape to peel graphene from HOPG</td>
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<td>Epitaxial growth on SiC</td>
<td>Good Control over number of layers Large domains</td>
<td>Expensive substrates High temperature Surface steps</td>
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<td>Anneal SiC (1200 – 1500°C) → Si sublimation</td>
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<td>Heat catalyst film and supply hydrocarbon (CVD: 530 – 1000°C; SWP-CVD: 300°C)</td>
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<td>Plasma assisted deposition on insulator (including this work)</td>
<td>Metal-free Large-area Directly on insulator</td>
<td>?</td>
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<td>Substrate exposed to carbon plasma</td>
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Thank you for your attention