Spring 3-13-2013


JR Dennison  
_Utah State University_

Jodie C. Gillespie  
_Utah State University_

Sterling Smith  
_General Atomics_

Follow this and additional works at: https://digitalcommons.usu.edu/mp_presentations  
Part of the Physics Commons

Recommended Citation  
https://digitalcommons.usu.edu/mp_presentations/33

JR Dennison,¹ Jodie Corbridge Gillespie, ¹ and Sterling Smith²

¹Materials Physics Group, Physics Department, Utah State University
²General Atomics
Graphite vs. Graphitic Amorphous Carbon

Accepted Graphene/Graphite Model:
- 1 D Planar Hexagonal Crystalline Structure
- Long Range Order
- Only 6-membered rings

Proposed g-C Model*:
- Very largely sp² bonding (narrow bond length distribution)
- Narrow bond angle distribution
- Distribution of ring sizes
- Warped planar (nearly 1D), continuous random network (CRN) with 10-20 nm rafts

* Beeman, PRB, 33, 1978.
Graphite vs. g-C: Short Range Order

**Coordination**
- Same

**Bond Length**
- Almost Same
  - 1.42±0.01 Å

**Bond Angle**
- Similar
  - 117±5 º

**Dihedral Angle**
- Somewhat Similar

**Ring Statistics**
- Different
  - 5-member
  - 6-member
  - 7-member

**Graphite vs. g-C:**
- % of Total

- g-C
- Graphite

- Ring Size
  - 5
  - 6
  - 7
**Graphitic Carbon: Sample Characterization**

**Surface Morphology:** SEM, Optical microscopy, STM

**Surface Contamination:** Auger Electron Spectroscopy

**Bulk Structure:** Raman Spectroscopy,

**Band Gap:** Photoyield Spectroscopy

**Density of States:** IR Reflection Spectroscopy

**Property** | **Graphite** | **Graphitic Amorphous Carbon**
--- | --- | ---
**Fabrication** | Highly Oriented Pyrolytic (HOPG) | Arc Evaporated*
**Density** | 2.267 g/cm³ | 1.82 g/cm³
**Surface Roughness** | <1 nm | < 1 nm
**Color** | Soft, black glossy | Soft, dull “sooty” black
**Resistivity** | 5×10⁻² Ω·cm (interlayer) 4×10⁻⁵ Ω·cm (basal plane) | 5×10⁻¹ Ω·cm
**Type** | Semi-metal | Semiconductor
**Band Gap** | 0.00 eV ± 0.05 eV | 0.65 eV ± 0.05 eV

Raman spectroscopy probes intermediate range order in Carbon

Use Thermal Annealing to Study a Structural Progression from $g$-G to Nanocrystalline Graphite/Graphene


Progression of Raman Spectra of PAH

As the size of Polycyclic Aromatic Hydrocarbon (PAH) molecules increases, the peaks for the Raman active 6-membered ring modes in the spectra approach those of graphite. *

$6 \text{A}_1g \text{ Mode}$

$1360 \text{ cm}^{-1}$

$6 \text{E}_2g \text{ Mode}$

$1581 \text{ cm}^{-1}$

Embedded Ring Approach (ERA)

Assumptions of the Embedded Ring Approach:\textsuperscript{1,2}

- The rings are regular polyhedra
- There is only planar sp\textsuperscript{2} bonding
- Force constants \( f_r \) and \( f_\theta \) fit to 6E\textsubscript{2g} and 6A\textsubscript{1g} modes
- Rings can be cleverly coupled to embedding CRN, \( f_c = 2 f_r \)
- For Raman spectra, looks only at in-plane modes

\textbf{A\textsubscript{1} modes only show up for finite crystal sizes.}

\begin{itemize}
  \item 5 \textit{A\textsubscript{1}} Mode \hspace{1cm} 6 \textit{A\textsubscript{1g}} Mode \hspace{1cm} 7 \textit{A\textsubscript{1}} Mode
  \begin{align*}
  \text{1444 cm}\textsuperscript{-1} & \hspace{1cm} 1360 \text{ cm}\textsuperscript{-1} & \hspace{1cm} 1303 \text{ cm}\textsuperscript{-1}
  \end{align*}
\end{itemize}

\textbf{E\textsubscript{2} modes Raman active even for infinite crystal.}

\begin{itemize}
  \item 5 \textit{E\textsubscript{2}} Mode \hspace{1cm} 6 \textit{E\textsubscript{2g}} Mode \hspace{1cm} 7 \textit{E\textsubscript{2}} Mode
  \begin{align*}
  1541 \text{ cm}\textsuperscript{-1} & \hspace{1cm} 1581 \text{ cm}\textsuperscript{-1} & \hspace{1cm} 1541 \text{ cm}\textsuperscript{-1}
  \end{align*}
\end{itemize}


g-C Annealed to 150 °C

Intensity (Arbitrary Units)

Raman Shift (cm⁻¹)

- Raw Data
- Fit
- 5 A Mode
- 5 E Mode
- 6 A Mode
- 6 E Mode
- 7 A Mode
- 7 E Mode

<table>
<thead>
<tr>
<th>Mode</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>31%</td>
</tr>
<tr>
<td>6</td>
<td>43%</td>
</tr>
<tr>
<td>7</td>
<td>26%</td>
</tr>
</tbody>
</table>
Temperature Dependence of Ring Statistics

**Ring Statistics Fits**

- Fraction of 6 member rings increases linearly with annealing T, up to ~900 °C
- Number of 5- and 7-membered rings nearly equal (±3%), as required for planar structures and Stone-Wallar defect pairs
- 4- and 8-membered rings do not improve fit
- Largely independent of Raman excitation energy
Graphite/Graphitic Carbon: Band Structure

ARPES of Graphite

(e,2e) spectra of annealed g-C
Ritter, Dennison, PRL (1984)
Presence of similar fine structure peak at $7\pm 1$ eV in all spectra indicates electronic structure is similar below $\sim 5$ eV for all carbon samples.

g-C Band Gap: Photoyield Spectra

Photoyield shows: Annealing T decreases bandgap toward 0 eV.

Increased N₆ decreases bandgap toward 0 eV.
Band Gap and Yield vs $N_6$ (or Annealing $T$)

Dependence on $N_6$

**Band Gap**

**Annealing $T$**

**Max SE Yield:**

$$\delta = \frac{I_{SE}}{I_{INCIDENT}}$$

**Energy of Max SE Yield:**

$$E_{\text{max}} \at \delta_{\text{max}}$$
Conclusions

- Embedded Ring Analysis of annealed g-C Raman spectra shows ring statistics provide a way to characterize amorphous structure

- \( N_6 \approx N_7 \approx 1/2(1-N_6) \) rings statistics scale linearly with annealing \( T \)

- Electronic Dispersion and DOS of g-C depend on annealing \( T \) or \( N_6 \)
  - Band gap \( (0<E_{\text{gap}}<0.65 \text{ eV}) \) decreases linearly with annealing \( T \)
  - Van Hove-like \( \sim 7 \text{ eV} \) and \( E_{\Gamma} \approx 21 \text{ eV} \) DOS features unaffected

- SE Emission and Yields (important for SEM) scale with bandgap, annealing \( T \), or \( N_6 \).
  - \( \delta_{\text{max}} \) for g-C linearly increases 30% for \( \sim 0.65 \text{ eV} \) increase in bandgap.
  - \( \delta_{\text{max}} \) for \( \geq 1050 \, ^\circ \text{C} \) annealed g-C same as graphite
  - Other material parameters (e.g., \( Z \), density, surface roughness or contamination) do not explain increased SE yield.

- Annealed g-C study shows sp\(^2\) warped planar island model of g-C is consistent with evolution of electronic, vibrational and structural data

- Structure and evolution of g-C Stone-Wallar-like defects provides an important model of a highly disordered limiting case of nearly planar graphite/graphene
Embedding of Rings
# Graphitic Carbon: Samples for Study

Graphite

Graphitic amorphous carbon (g-C)

Annealing at:
- 350 °C
- 650 °C
- 850 °C
- 1050 °C

<table>
<thead>
<tr>
<th>Property</th>
<th>HOPG</th>
<th>g-C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density</strong></td>
<td>2.267 gm/cm³</td>
<td>1.82 gm/cm³</td>
</tr>
<tr>
<td><strong>Surface Roughness</strong></td>
<td>&lt;1 nm</td>
<td>&lt; 1 nm</td>
</tr>
<tr>
<td><strong>Resistivity</strong></td>
<td>5 x10⁻² S-cm (interlayer)</td>
<td>5x10⁻¹ S-cm</td>
</tr>
<tr>
<td></td>
<td>4 x10⁻⁵ S-cm (basal plane)</td>
<td></td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>Semi-metal</td>
<td>Semiconductor</td>
</tr>
<tr>
<td><strong>Band Gap</strong></td>
<td>0.00 eV ± 0.05 eV</td>
<td>0.65 eV ± 0.05 eV</td>
</tr>
</tbody>
</table>
The SE and BSE yields are ratios of the number of electrons emitted for each incident electron as:

**SE Yield:** \[ \delta = \frac{I_{SE}}{I_{INCIDENT}} \]

**BSE Yield:** \[ \eta = \frac{I_{BSE}}{I_{INCIDENT}} \]

Plots of the SE (above) and BSE (left) yields as a function of incident beam energy are shown for a conducting material (Au) along with various fits. For the SE yield, the two energies for which the yield equals one are called the first and second crossover energies, \( E_1 \) and \( E_2 \). Additionally, the maximum yield, \( *_{max} \) and corresponding energy, \( E_{max} \) are important material charging parameters.
Semiconductor theory must be inferred from qualitative insulator theory

**Metals:**
- Low SE yields
- Electron-electron scattering dominates transition
- Work function is surface barrier

**Large bandgap insulators:**
- High SE yields
- Phonon and recombination dominate scattering.
- Bandgap inhibits electron-electron scattering near the conduction band minimum increasing mean free path
- Electron affinity is surface barrier

\[
\delta(E) = \int_0^R B \left[ e^{-x/\lambda} \right] \left[ \left( \frac{A}{\varepsilon} \right) \frac{1}{E^{n-1}} \right] \, dx
\]
Graphitic Carbon: SE Yield

- g-C 30% higher $\delta_{\text{max}}$ than HOPG
- 1050 °C g-C has same $\delta_{\text{max}}$ as HPOG
- Measurements of other annealed g-C in progress