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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 sp$^2$ 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**: 1.42±0.01 Å, Almost Same
- **Bond Angle**: 117±5 °, Similar
- **Dihedral Angle**: Somewhat Similar

**Ring Statistics**

- 5-member
- 6-member
- 7-member

**% of Total**

<table>
<thead>
<tr>
<th>Ring Size</th>
<th>g-C</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Different
## Graphitic Carbon: Sample Characterization

### Surface Morphology:
- SEM, Optical microscopy, STM

### Surface Contamination:
- Auger Electron Spectroscopy

### Bulk Structure:
- Raman Spectroscopy
- Photoyield Spectroscopy
- IR Reflection Spectroscopy
- Electron Emission Spectroscopy and Yields (e,2e) Electron Spectroscopy

### Band Gap:
- Graphite: 0.00 eV ± 0.05 eV
- Graphitic Amorphous Carbon: 0.65 eV ± 0.05 eV

### Density of States:
- Electron Emission Spectroscopy and Yields (e,2e) Electron Spectroscopy

### Fabrication
- Highly Oriented Pyrolytic (HOPG)
- Arc Evaporated

### Density
<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite</th>
<th>Graphitic Amorphous Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabrication</td>
<td>Highly Oriented Pyrolytic (HOPG)</td>
<td>Arc Evaporated*</td>
</tr>
<tr>
<td>Density</td>
<td>2.267 g/cm³</td>
<td>1.82 g/cm³</td>
</tr>
<tr>
<td>Surface Roughness</td>
<td>&lt;1 nm</td>
<td>&lt; 1 nm</td>
</tr>
<tr>
<td>Color</td>
<td>Soft, black glossy</td>
<td>Soft, dull “sooty” black</td>
</tr>
<tr>
<td>Resistivity</td>
<td>5 x 10⁻² Ω-cm (interlayer) 4 x 10⁻⁵ Ω-cm (basal plane)</td>
<td>5 x 10⁻¹ Ω-cm</td>
</tr>
<tr>
<td>Type</td>
<td>Semi-metal</td>
<td>Semiconductor</td>
</tr>
</tbody>
</table>

Raman Spectra of Carbon Structures

Raman spectroscopy probes intermediate range order in Carbon

Diamond
CVD Microcrystalline Diamond Film
Single Crystal Graphite
Nanocrystalline Graphite/Graphene
Arc Evaporated Graphitic Amorphous Carbon
Ion Sputtered Graphitic Amorphous Carbon
Powdered C_{60}

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. *

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 $6E_{2g}$ and $6A_{1g}$ modes
- Rings can be cleverly coupled to embedding CRN, $f_c=2f_r$
- For Raman spectra, looks only at in-plane modes

\begin{itemize}
\item \textbf{A\textsubscript{1} modes only show up for finite crystal sizes.}
\item \textbf{E\textsubscript{2} modes Raman active even for infinite crystal.}
\end{itemize}


g-C Annealed to 150 °C

Intensity (Arbitrary Units)

Raman Shift (cm$^{-1}$)

- 5 E Mode
- 5 A Mode
- 6 E Mode
- 6 A Mode
- 7 A Mode
- 7 E Mode

Raw Data

Fit

Bar chart:

- 5: 31%
- 6: 43%
- 7: 26%
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

$E_{\text{gap}} = 0 \text{ eV}$

$E_{\text{peak}} = \sim 7 \text{ eV}$

$E_{\text{min}} = \sim 21 \text{ eV}$

ARPES of Graphite


(e,2e) spectra of annealed g-C

Ritter, Dennison, PRL (1984)
Presence of similar fine structure peak at 7±1 eV in all spectra indicates electronic structure is similar below ~5 eV for all carbon samples.

g-C Band Gap: Photoyield Spectra

Photocurrent shows: Annealing T decreases bandgap toward 0 eV.
Increased N₆ decreases bandgap toward 0 eV.
Band Gap and Yield vs N₆ (or Annealing T)

**Dependence on N₆**

**Band Gap**

**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

- \( N_6 \) and \( N_5 \approx N_7 \approx \frac{1}{2}(1-N_6) \) rings statistics scale linearly with annealing \( T \)

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

- SE Emission and Yields (important for SEM) scale with bandgap, annealing \( T \), or \( N_6 \).
  - \( \delta_{max} \) for g-C linearly increases 30% for \( \sim 0.65 \text{ eV} \) increase in bandgap.
  - \( \delta_{max} \) 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

- **Density:** 2.267 gm/cm³
- **Surface Roughness:** <1 nm
- **Resistivity:**
  - Interlayer: $5 \times 10^{-2}$ S-cm
  - Basal plane: $4 \times 10^{-5}$ S-cm
- **Type:** Semi-metal
- **Band Gap:** $0.00 \text{ eV} \pm 0.05 \text{ eV}$

#### Graphitic amorphous carbon (g-C)

- **Density:** 1.82 gm/cm³
- **Surface Roughness:** <1 nm
- **Resistivity:**
  - Interlayer: $5 \times 10^{-1}$ S-cm
  - Basal plane: $4 \times 10^{-5}$ S-cm
- **Type:** Semiconductor
- **Band Gap:** $0.65 \text{ eV} \pm 0.05 \text{ eV}$

#### Annealing
- 350 °C
- 650 °C
- 850 °C
- 1050 °C

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**Table:**

<table>
<thead>
<tr>
<th>Property</th>
<th>HOPG</th>
<th>g-C</th>
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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, \( *_{\text{max}} \), and corresponding energy, \( E_{\text{max}} \), 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

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

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