Electron beam generated plasmas:
Ultra cold sources for low damage, atomic layer processing

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Motivation

As material demands evolve toward the single nanometer-scale dimensions, one would like to systematically modify one and only one monolayer at a time, without "damaging" other layers.

Atomic layer etching/deposition

2-D material processing

Polymer processing

Plasma Requirements

- Precise control over the flux of species and the ion energy at surfaces during processing
- For very thin materials (e.g. 2-D materials), the energy of incident ions should be low as possible to minimize damage while processing

Electron Beam Generated Plasmas

• Unique control over species production
• Inherently low electron temperature and thus, uniquely low ion energies
Electron beam generated plasma processing system

Large Area Plasma Processing System (LAPPS)*

**Basic Operation**
- High energy beam injected into background
- Creates Plasma
  - Ionizes: Charged Particles (ions and electrons)
  - Excites: Species emit photons
  - Dissociates: Reactive Radicals

*Meger et al., US patent no. 5,874,807 (Feb. 1999)
Platforms for processing

Source is decoupled from reactor geometry

- Flexible design
- Unique geometries

PEPVD*

Magnetized or not

Roll to Roll**

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Platforms and processing

• Scaling is straightforward to accommodate large area processing
  – width scales with e-beam source width
  – length scales with beam energy and pressure

Electron beam range in N₂

Large area rectangular chamber (1 m² capability)
Platforms and processing

- Source is scalable to large areas without losses in uniformity

Model Validation

Prototype System

- $n_e$ (Max. = $1.74 \times 10^{17}$ m$^{-3}$)
- $T_e$ (Max. = 1.02 eV)

S. Rauf et al., AVS International Symposium, San Jose, CA (October 18-23, 2015)
Plasma generation with high-energy electron beams

• In discharges,
  • electric fields to energize plasma electrons
  • small fraction of electrons ionize gas
  • most energy is used to excite the gas

• The injection of a 2 keV beam into the background gas will directly ionize and dissociate the gas.
  • more efficiently ionize
  • no threshold determination
  • ionize all species equally

• The plasma (or secondary) electrons have much a lower energy
  • are not required to sustain the plasma
  • cooled electrostatically and through inelastic collisions

... the resulting plasmas have unique features
Unique Features of Electron Beam-Generated Plasmas

Simple Control of plasma density and species production

\[ \frac{dn_i}{dt} = S_i - L_i = 0 \]

\[ S_i = k I_{beam} P_i \sigma_i \]

Plasma density scales with beam current

Unique Features of Electron Beam-Generated Plasmas

Species generation is proportional to the relative concentrations of the working gases

\[ S_i = k I_{\text{beam}} P_i \sigma_i(E) \]

**Unique Features of electron beam generated plasmas**

$T_e$ is low and dependent on background gas

![EEDF in beam channel](image)

$E_{\text{EDF}}$ cools with increasing nitrogen concentration

Leading to a corresponding drop in $T_e$

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Unique Features of electron beam generated plasmas

Very low $T_e$ provides very low ion energy

**IED at Electrode surface**

Plasma Potential:

$$V_p = T_e \ln(M_i/2\pi m_e)^{1/2}$$

Ion Energy:

$$E_{ion} = V_p - V_{sb}$$


Unique Features of electron beam generated plasmas

**Electron Beam Generated Plasmas** have a fundamentally low $T_e$ (even at high plasma densities) and thus provide a large flux of low energy ions.

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**Electron Density** (cm$^{-3}$)

**Average Electron Energy** (eV)

**Plasma sources (discharges) used in materials processing**

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_e$ (eV)</th>
<th>$n_e$ (cm$^{-3}$)</th>
<th>KE$_{ion}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP</td>
<td>4</td>
<td>$10^{11}$</td>
<td>20</td>
</tr>
<tr>
<td>ECR</td>
<td>4</td>
<td>$10^{11}$</td>
<td>20</td>
</tr>
<tr>
<td>DBD</td>
<td>2 - 10</td>
<td>$10^{13}$</td>
<td>10 - 100</td>
</tr>
<tr>
<td>RIE</td>
<td>8</td>
<td>$10^{10}$</td>
<td>40</td>
</tr>
<tr>
<td>DC Diode</td>
<td>2 - 10</td>
<td>$10^{10}$</td>
<td>10 - 100</td>
</tr>
<tr>
<td>CCP</td>
<td>1 - 5</td>
<td>$10^9$-$10^{10}$</td>
<td>5 - 25</td>
</tr>
<tr>
<td><strong>Electron Beam</strong></td>
<td><strong>0.3 - 1</strong></td>
<td><strong>$10^9$-$10^{12}$</strong></td>
<td><strong>1.5 - 5</strong></td>
</tr>
</tbody>
</table>

Processing implications

Electron beam generated plasmas provide:
- Unique control over the production of species and their transport to surface
- \( n_e \) is high \( (10^{10} - 10^{11} \text{ cm}^{-3}) \); \( T_e \) is very low \( (\approx 0.5 \text{ eV}) \)
- In the absence of any biasing, a mix of reactive species in concert with a large flux of very low energy \((0 - 5 \text{ eV})\) ions

Ion-induced surface processes*

Processing implications: Low damage

Low ion energy is valuable in maintaining crystallinity

Chemical Modification of Ion Energy Sensitive Materials

- Chemical modification without physical changes (e.g. surface roughening)
- Polymers or other “soft” materials
- Sensors and biomaterials applications

Atomic Layer Modification

- Graphene Oxide Reduction – reduction to graphene without damage
- Graphene (or other 2-D materials) functionalization - etching is not an option
- Sensors and electronic applications

Atomic Layer Etching

- Selective removal of only one monolayer at a time
- Polymers (e.g. photoresist)
- Silicon
- Metal and/or silicon oxide/nitrides
- Microelectronics applications
Graphene
Processing
Functionalized Graphene: Chemical Modification

Graphene on Si/SiO₂ *

Epitaxial Graphene on SiC **

Controllably introduce functional groups

![Graphene on Si/SiO₂](image1)

![Epitaxial Graphene on SiC](image2)

**M. Baraket, et al., Appl. Phys. Lett. 96 231501 (2010).**

Functionalized Graphene; Functional Surfaces

- Exposure to ammonia-containing plasmas leads to the incorporation of both primary amines (NH$_2$) and N
- Surface reactivity increases and sheet resistance remains reasonably low

![Graph showing primary amine coverage and sheet resistance and reactivity over nitrogen coverage](image-url)
Functionalized Graphene: Enhanced atomic layer deposition (ALD)

ALD of $\text{Al}_2\text{O}_3$ on fluorinated epitaxial graphene

- 20nm of $\text{Al}_2\text{O}_3$
- Conformal oxide layer only on the functionalized regions

ALD of $\text{HfO}_2$ on fluorinated CVD graphene*

Large difference between source-drain current ($I_{CH}$) and source-gate current ($I_G$) indicate successful isolation of graphene

Functionalized Graphene: Controlling the properties at contacts

In collaboration with Prof. Patrick Hopkins (UVA)

Chemical Patterning of Graphene

Direct chemical patterning of graphene for greater control over material properties and reactivity

Physical masking technique + plasma functionalization

S. C. Hernández et al., Carbon 60, 84 (2013)
Chemical Patterning of Graphene: Gradients

Producing chemical gradients on graphene

- Canopy mask + plasma functionalization to produce chemical gradients
  - Continuous in gradient direction (x) and uniform laterally (y)
  - Flexibility in chemistry to grade the surface reactivity

Chemical Patterning of Graphene: Gradients

Oxygen gradient for “pulling” $H_2O$

Atomic Layer Etch
CNT Etching: A comparative study

Compare the response of semiconducting CNT’s to CH₄ plasmas

E-beam generated plasma + 10 V surface bias

- Ion decreases
- I_{off} remains similar
- Semiconducting properties generally retained

Low power ICP etch tool + 25 W surface bias

- Ion decreases
- I_{off} increases
- Semiconducting properties \textit{not} generally retained

Results show less damage (D/G ratio) to the graphene after e-beam plasma etch compared to ICP etching.

Electron Beam Generated Plasmas

- Unique control over the production of species and their transport to surface
- \( n_e \) is high \((10^{10} - 10^{11} \text{ cm}^{-3})\); \( T_e \) is very low \((\approx 0.5 \text{ eV})\)
- Large flux of very low energy \((0 - 5 \text{ eV})\) ions
- Well-suited to advance unique processing applications
  - Ion energy-sensitive materials
  - Atomic Layer Etch (or Deposition)
  - Processing of very thin \((\sim \text{ nm})\) or atomically thin \((2\text{-D})\) materials
Thank you

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