Utilizing Massively-Parallel Computations to Predict Nanopatterning of Graphene by Plasma-Surface Interaction

Huck Beng Chew (PI)
Abhilash Harpale (former Ph.D. student; currently at Intel)

Department of Aerospace Engineering
University of Illinois at Urbana-Champaign

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Blue Waters

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Motivation: Scalable Graphene Patterning

Graphene-Based Products and Devices

- Bandgap Opening
- Gas Purification
- DNA Sequencing
- Water Filtration

Dvorak et al. (2013)

Cohen-Tanugi and Grossman (2012)

Hauser and Schwerdtfeger (2012)

Postma (2010)
Background: Hydrogen-Plasma Treatment

- What are the etching mechanisms?
- Can we control them to achieve the desired nanopatterned structure?

Felten et al. (2014)

Downstream distance

H ions, radicals

Monolayer graphene

SiO₂ substrate

Inductive plasma

H ions and radicals


Xie et al. (2013)

(2013)  g et al. (2010)
Insights from MD Simulations

Molecular Dynamics Simulations with ReaxFF (Si-C-O-H) potential

\[ E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \]

H ions, radicals

Monolayer graphene

SiO$_2$ substrate
Insights from MD Simulations

Molecular Dynamics Simulations with ReaxFF (Si-C-O-H) potential

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}
\]

Pristine graphene

\[
a = 1.424 \text{ Å (DFT)}
\]

\[
a = 1.443 \text{ Å (ReaxFF)}
\]

C-H bonding structure

Barrier energy for H penetration

<table>
<thead>
<tr>
<th>Property</th>
<th>DFT</th>
<th>ReaxFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H bond length</td>
<td>1.08–1.17 Å</td>
<td>1.11 Å</td>
</tr>
<tr>
<td>C-C bond length</td>
<td>1.49–1.51 Å</td>
<td>1.50 Å</td>
</tr>
<tr>
<td>ΔZ of C atom</td>
<td>0.47–0.53 Å</td>
<td>0.35 Å</td>
</tr>
<tr>
<td>C-C-H angle</td>
<td>101.3 deg</td>
<td>104.6 deg</td>
</tr>
<tr>
<td>C-C-C angle</td>
<td>115.4 deg</td>
<td>113.9 deg</td>
</tr>
</tbody>
</table>

Chemisorption energy

DFT: \( \Delta E = 0.6 – 1.44 \text{ eV} \)

ReaxFF: \( \Delta E = 0.51 – 1.65 \text{ eV} \)

Equilibrium distance

Graphene – SiO₂

DFT: \( Z = 2.90 \text{ Å} \)

ReaxFF: \( Z = 2.84 \text{ Å} \)
Insights from MD Simulations

Molecular Dynamics Simulations with ReaxFF (Si-C-O-H) potential

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} +$$

$$E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

H$^+$ energy

1 eV  5 eV  10 eV  25 eV

H ions

Monolayer graphene

SiO$_2$ substrate
Insights from MD Simulations

Etching Mechanisms

- Selective Edge Etching
- Isotropic Basal Plane Etching
- Anisotropic Basal Plane Etching

Kinetics of Early-Stage Plasma Etching

Experimentally-Relevant Length- and Time-Scales

Scale-Bridging

1 eV

25 eV

Edge-Etching

Combined Edge & Basal Plane Etching

Edge-Etching
Basal Plane Etching: Damage Nucleation

Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

C-C bonds stretched to 1.7 Å

Baseline-plane etching rate $\dot{D}_b$

$D_b = \text{Fraction of C-C bonds broken}$

Selective edge etching

Preferential hydrogenation sites to form CH$_2$ and CH$_3$
**Edge Etching: Damage Propagation**

Scale-Bridging MD Simulations

**Kinetics of Early-Stage Plasma Etching**

- High edge reactivity
- High C-C bond strength

**Chemical reactivity of edge atoms versus bond strength**

- Edge-etching rate $\dot{D}_e$

![Diagram showing zigzag etching and a graph with isotropic and anisotropic etching rates as functions of ion energy.](image)
Edge Etching: Damage Propagation

Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

Chemical reactivity of edge atoms versus bond strength

Edge-etching rate $\dot{D}_e$

- Low edge reactivity
- Low C-C bond strength
Isotropic Edge Etching

Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

Chemical reactivity of edge atoms versus bond strength

Edge-etching rate $\dot{D}_e$

Fluence

Armchair etching

Bond breaking

Edge hydrogenation

Armchair edge

Zigzag edge

$C_n = na_1 + ma_2$

(n,0) zigzag

(n,n) armchair
Isotropic Edge Etching

Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

Chemical reactivity of edge atoms versus bond strength

Edge-etching rate $\dot{D}_e$
Anisotropic Edge Etching

Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

Chemical reactivity of edge atoms versus bond strength

Edge-etching rate $\dot{D}_e$

Fluence

Armchair edge

Zigzag edge

Bond breaking

Ion energy (eV)

$D_e = \frac{dD_e}{d\delta}$ (cm)

Armchair

Zigzag

Bond breaking
Anisotropic Edge Etching

Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

Chemical reactivity of edge atoms versus bond strength

Edge-etching rate $\dot{D}_e$
Scale-Bridging MD Simulations

Kinetics of Early-Stage Plasma Etching

<table>
<thead>
<tr>
<th>No. of etched C atoms</th>
<th>Basal plane etching</th>
<th>Edge etching</th>
<th>Ion fluence (ions/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole radius R</td>
<td>( \dot{D}_b ) (2\pi R)</td>
<td>( \dot{D}_e ) (2\pi R)</td>
<td>( \frac{\alpha \dot{D}_e}{\dot{D}_b} \ln \left( 1 - \frac{\dot{D}_e R}{\dot{D}_b R} \right) )</td>
</tr>
</tbody>
</table>

1D-Micromechanics Model

Experimentally-Relevant Length- and Time-Scales
Monolayer Graphene: Selective Edge Etching

Bridging Simulations and Experiments

Kinetics of Early-Stage Plasma Etching

20 W, 40 cms
~ 0.27 nm/min

Ion energy: 1 eV

3 Distinct Plasma-Graphene Reactions
Monolayer Graphene: Isotropic Hole Growth

Bridging Simulations and Experiments

Kinetics of Early-Stage Plasma Etching

20 W, 30 cms
~ 40 nm/min
Ion energy: 2 eV

Basal-plane etching rate $\dot{D}_b$
Edge-etching rate $\dot{D}_e$

$R = -\frac{\alpha \dot{D}_e}{\dot{D}_b} \ln \left( 1 - \frac{\dot{D}_b \xi}{\rho} \right)$

40 nm/min etch rate

3 Distinct Plasma-Graphene Reactions
Monolayer Graphene: Anisotropic Hole Growth

Bridging Simulations and Experiments

Kinetics of Early-Stage Plasma Etching

Ion energy: 25 eV

50 W, 40 cms

~ 8 nm/min

6 nm/min etch rate

3 Distinct Plasma-Graphene Reactions

Basal-plane etching rate $\dot{D}_b$

Edge-etching rate $\dot{D}_e$

$R = -\frac{\alpha \dot{D}_e}{\dot{D}_b} \ln \left( 1 - \frac{\dot{D}_b \xi}{\rho} \right)$

30 eV

25 eV

20 eV

3 eV

2 eV

1 eV

Fluence $\xi$ (ions cm$^{-2}$)

Radius $R$ (nm)
Role of Blue Waters Computations

Controlling Patterning of Graphene

- Selective Edge Etching
- Isotropic Basal Plane Etching
- Anisotropic Basal Plane Etching

Graphene Nanostructure

3 Distinct Plasma-Graphene Reactions

Plasma Process Conditions

$R = -\frac{\alpha \hat{D}_e}{\hat{D}_b} \ln \left(1 - \frac{\hat{D}_b \xi}{\rho}\right)$

Ion Energy vs. Fluence $\xi$ (ions cm$^{-2}$)

Ion Energy: 1 eV, 2 eV, 3 eV, 20 eV, 25 eV, 30 eV

Fluence $\xi$: 0.0 to 1.5 $\times 10^{18}$
Role of Blue Waters Computations

Controlling Patterning of Graphene

3 Distinct Plasma-Graphene Reactions

- Selective Edge Etching
- Isotropic Basal-Plane Etching
- Anisotropic Basal-Plane Etching

Graphene Nanostructure

Computational effort:
~30k CPU hours
~10 days on 128-core machine for each data point

\[ R = -\frac{\alpha \dot{D}_e}{\dot{D}_b} \ln \left( 1 - \frac{\dot{D}_b}{\rho} \xi \right) \]
Controlling Patterning of Graphene

1. Experimental / Physical Observation

2. Computational Tools

3. Develop Models to Predict / Explain Phenomena

\[ R = -\frac{\alpha \hat{D}_e}{\hat{D}_b} \ln \left( 1 - \frac{\hat{D}_b \xi}{\rho} \right) \]

4. Application


Blue Waters Computations: Enabling Science in Mechanics

Graphene Transistors