Atomistic Modeling of Graphene Nanostructures

Junzhe Geng

Committee: Prof. Gerhard Klimeck (Chair)
Prof. Mark Lundstrom, Prof. Timothy Fisher
Outline

• Introduction/Motivation
  » Why graphene is important
  » Challenges for graphene applications
  » Graphene nanostructures

• Model Details
  » Nearest neighbor tight-binding model in graphene
  » Need for P/D model

• Modeling of Graphene Nanomeshes (GNM)
  » Circular hole GNM: Bandgap & edge states
  » Rectangular hole GNM: Anisotropic conductance

• Conclusion and Future Work
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Device performance enhancement has mainly come from CMOS downscaling in the past few decades.

CMOS scaling is fundamentally limited by several technological issues, such as short channel effects.

Channel length of today’s CMOS is close to such scaling limit of sub-10 nm.
• Giant intrinsic mobility
  » Over 15,000 cm²/V-s measured, upper limit predicted to be over 100,000 cm²/V-s
  » Weak dependence on temperature and charge density

• Support high current density

• High thermal conductivity

• Outstanding Mechanical properties: strength, stiffness, etc.
Why Graphene Electronics?

**Good high-field transport**
- Device performance at small gate length is measured by high-field transport characteristics
- Graphene has much higher electron velocity compared to other semiconductor materials
- The electron velocity in graphene doesn’t decrease much in the high field
- Graphene is ideal for high-speed applications, such as RF devices

**The 2D nature**
- Graphene makes extremely thin channel, which prevents off current
- Single atomic layer channel represents the ultimate limit of channel thickness

Image from: University of Maryland
Although graphene applications has seen rapid progresses, they are still limited mostly to radiofrequency devices.

- Large area graphene sheet has zero banggap → Devices cannot be fully turned off → large leakage power.
- The biggest challenge in graphene applications is opening up a bandgap!
Bandgap opening techniques

Nanoribbon


Biased Bi-layer Graphene


Epitaxial graphene on SiC


Apply strain in Graphene

NEMO5

W = 3.3 nm
E_g = 0.25 eV

W = 1.1 nm
E_g = 1.13 eV

Bandgap opens up in GNR due to lateral confinement, \( E_g \sim 1/w^\alpha \), with \( \alpha \approx 1 \)


\( I_{on}/I_{off} > 10^5 \)
**Drawbacks of GNR:**

- Lithographical challenges
  - Very narrow nanoribbons (W < 10 nm), well-defined edges are necessary
- Low driving current
  - Practical devices or circuits require production of dense arrays of GNR

**The Alternative: Graphene nanomesh (GNM)**

**Advantages of GNM:**

- Easier to process, effectively a dense array of GNR
- Large driving current
- Tunable bandgap

Currently obtainable on-off ratio ~ 100

Objectives of this work

• Investigate the properties of Graphene Nanomesh using the computational modeling approach
  » How does the geometry (hole size, shape) affect electronic properties?
  » Can we engineer the electronic structure of GNM?
  » Is GNM fit for nanoelectronics applications?

• Methodology: Nearest neighbor tight-binding model
  » The GNM structures to be modeled contain hundreds of atoms
  » Tight-binding method is good at handling such large computational intensive tasks, and reproducing the essential physics
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Graphene Lattice and Brillouin Zone

Lattice basis:
\[ \vec{a}_1 = \frac{3a_0}{2} \hat{x} + \frac{\sqrt{3}a_0}{2} \hat{y} \]
\[ \vec{a}_2 = \frac{3a_0}{2} \hat{x} - \frac{\sqrt{3}a_0}{2} \hat{y} \]

Reciprocal lattice basis:
\[ \vec{A}_1 = \frac{2\pi}{3a_0} \hat{x} + \frac{2\pi}{\sqrt{3}a_0} \hat{y} \]
\[ \vec{A}_2 = \frac{2\pi}{3a_0} \hat{x} - \frac{2\pi}{\sqrt{3}a_0} \hat{y} \]

Symmetry points:
\[ K : \frac{1}{3} \vec{A}_1 - \frac{1}{3} \vec{A}_2 \]
\[ M : \frac{1}{2} \vec{A}_1 \]
The $p_z$ orbital is well separated in energy from the $sp^2$ orbitals.

More importantly, only the $p_z$ electron is close to the Fermi level.

Therefore, the common tight-binding method for graphite/graphene considers only the $p_z$ orbital (P.R. Wallace, PRB 1947).
The pz tight-binding Model

\[ E\{\phi\} = [h(\vec{k})]\{\phi\} \]

\[ [h(\vec{k})] = \sum_m [H_{nm}] e^{i\vec{k} \cdot (\vec{d}_m - \vec{d}_n)} \]

- \{\Phi\}: (2 x 1) vector; [H]: (2 x 2) matrix
- since there are 2 orbitals per unitcell

\[
\left[ h(k) \right] = \begin{bmatrix}
\varepsilon & -t \\
-t & \varepsilon \\
\end{bmatrix} + \begin{bmatrix}
0 & 0 \\
0 & 0 \\
\end{bmatrix} e^{i\vec{k} \cdot \vec{a}_1} + \begin{bmatrix}
0 & 0 \\
0 & -t \\
\end{bmatrix} e^{i\vec{k} \cdot \vec{a}_2} + \begin{bmatrix}
0 & -t \\
0 & 0 \\
\end{bmatrix} e^{i\vec{k} \cdot \vec{a}_3} + \begin{bmatrix}
0 & -t \\
0 & 0 \\
\end{bmatrix} e^{i\vec{k} \cdot \vec{a}_4} \\
\]

\[
\left[ h(k) \right] = \begin{bmatrix}
\varepsilon \\
h_0(k) \\
\end{bmatrix} \begin{bmatrix}
h_0(k) \\
\varepsilon \\
\end{bmatrix} \]

\[ E = \pm \left[ h_0(k) \right] \] (if \( \varepsilon = 0 \))

\[ = \pm t \sqrt{1 + 4 \cos k_y b \cos k_x a + 4 \cos^2 k_y b} \]
• Features of graphene bandstructure
  » Conduction and valence bands cross at K points of Brillouin zone, forming Dirac cones
  » At M points in the Brillouin zone, band edges are symmetric around the Dirac point (since $E = \pm |h_0(k)| \uparrow$ is symmetric around $E = 0$ eV)
• Flaws of the $p_z$ model
  » Could not reproduce the asymmetry of bands
  » Does not allow proper hydrogen passivation scheme. This is because the single $s$ orbital of hydrogen atom does not have any coupling to the $p_z$ orbital of carbon atom

• The solution: P/D model
  » Use a set of three orbitals \{p_z, d_{yz}, d_{zx}\} to represent each C atom
  » For hydrogen passivation, also use \{p_z, d_{yz}, d_{zx}\} to represent H atom

\[ E(\text{eV}) \]

\( \begin{align*}
\text{Gamma} & \quad \text{K} & \quad \text{M} \\
-3 & \quad 0 & \quad 3 \\
\end{align*} \)
Model validation: zig-zag nanoribbon

- P/D model correctly reproduces the band bending around the $E = 0$ eV.
- As a result, transmission has a ‘spike’, i.e., $T(E \approx 0) = 3$. This matches with DFT results.

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• Periodic structure in 2D
• Edges are passivated by H atoms
• Size of a supercell is 12 graphene primitive unit cells long, or 2.95 nm
• Hole diameter is varying
GNM: Bandstructure

E\(_g\) = 0.29 eV

d = 3uc

E\(_g\) = 0.56 eV

d = 5uc

E\(_g\) = 0.68 eV

d = 6uc

E\(_g\) = 0.75 eV

d = 7uc

Flat bands in the middle of the bandgap
• As hole size get bigger, flat bands appear in the middle of the bandgap

• Flat bands are edge states, where electron wavefunctions localize on the hole edge

• A closer look at the edge state reveals that wavefunctions tend to localize on the zigzag edge
• At small neckwidth range, bandgap is nearly inversely proportional to neckwidth.

• However, as hole size increases, edge effects become more prominent, which induces more localized states (flat bands) in the bandgap.

• As a result, bandgap results deviates from the linear trend at narrow neckwidth.

**Short Conclusion**

• Graphene with periodic perforation can open up sizeable bandgap, which makes GNM potentially useful for transistor applications.

• However, just like GNR, edge still plays an important role in electronic properties of GNM.
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• From previous study, it is learned that edges play a significant role in the band structure.
• Thus we can expect that different hole geometries lead to different E-k characteristics and electronic properties.
• Compare electronic properties between two types of structures “AGNM” and “ZGNM.”
• Dispersion of E-k is significantly larger along the hole direction, i.e., [010] for AGNM and [100] for ZGNM
• Many flat bands in the ZGNM bandstructure
• Flat bands are localized states on the zigzag edge
Anisotropic dispersion ➔ Anisotropic transmission
• High (low) dispersion ➔ High (low) transmission
• A rectangular hole serves as a ‘guide’ to electron conductance
• How does the edge affect electron conductance?
Same as before, electron wavefunction is localized on the zigzag edge.
Edges play an important role in GNM's electronic properties.
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Conclusion:
• Periodic perforations in graphene can open up a sizeable bandgap, making it possible for transistor applications
• The electronic properties of GNM are highly dependent on hole size and geometry. This opens up opportunities for bandstructure engineering in GNM.
• However, atomic precision lithography is still necessary to harness the potential of GNM, since the electronic properties depend heavily on the edge structure

Future Work:
• Full transport simulation with applied bias
• Propose novel device applications utilizing GNM properties, such as band-to-band-tunneling transistors
• Reliability test including edge roughness, hole size fluctuation, tilted angle, etc.
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