Probing optical and electronic properties of individual defects through scanning transmission electron microscopy and first-principles theory

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Advances in aberration correction

Pt on $\gamma$-Al$_2$O$_3$

P.D. Nellist 1996

Uncorrected

VG Microscopes HB603U 300 kV

A. Y. Borisevich 2004

3$^{rd}$ order corrected

Wu Zhou 2012

5$^{th}$ order corrected

Nion UltraSTEM 60 kV

Pt on graphene

1 nm
Stacking Sequence at Interfaces by STEM/EELS

Outline

• Point defects in graphene
  – Configuration
  – Bonding, electronic structure
  – Dynamics

• Optical properties
  – “Plasmons” in graphene
  – Atomic resolution valence EELS: optical properties defect by defect!

• Future directions
  – meV resolution EELS
  – 3D atomic resolution
Graphene team

Wu Zhou        Juan-Carlos Idrobo        Myron Kapetanakis        Jaekwang Lee

Single atom microscopy: Bonding, Dynamics and Optical Properties

Sok Pantelides
Tracking point defect dynamics

Direct identification of species from image intensity

Atom by atom spectroscopy
Revealing the nature of chemical bonding

How do the Si atoms bond in the graphene lattice?
Reference spectra for the Si L-edge

Si with sp\(^3\) hybridization

![Graph showing reference spectra for Si L-edge with different materials: Si, SiC, Si\(_3\)N\(_4\), and SiO\(_2\).]
Some 3d states in Si-C₄ structure are missing!
3D structure from DFT calculations

0.54 Å out-of-plane for Si-C$_3$
0.63 Å out-of-plane for SiC bulk

$sp^3$-like hybridization for Si-C$_3$

Myron Kapetanakis
Participation of $d_{xy}$ states in chemical bonding of Si-C$_4$

$3d_{xy}$

Si $3d_{xy}$ states participate in the chemical bonding of Si-C$_4$

$sp^2d$ hybridization for planar 4-fold coordination

Si$_6$ magic cluster

UltraSTEM at 60 kV

W. Zhou, J-C Idrobo: Si on graphene
Reversible dynamics at the atomic scale

Turn to theory: Jaekwang Lee
Atomic scale molecular dynamics

Optical properties from EELS

Energy loss: \( \chi(E) = \text{Im} \left( \frac{1}{\varepsilon(E)} \right) \)

\( \chi(E) \rightarrow \varepsilon(E) \rightarrow \varepsilon_1(E), \varepsilon_2(E) \)

Optical absorption

STEM-EELS: Optical absorption with atomic resolution
Delocalization is a problem?

Typical “plasmon” peaks of monolayer graphene

How do point defects affect the plasmon response?
Atomically localized plasmon enhancement

FWHM for enhanced plasmon: 0.43±0.05 nm (< λ/200)

Atomically localized plasmon resonance

Z-contrast plasmon (11-18 eV)

High frequency ($10^{15}$ Hz) signals could be transmitted along atomically confined paths by assembling single atoms on graphene

Use grain boundaries?
1-D edge plasmon on graphene with 6Å localization

Localization depends both on the energy loss and the specific electron excitation mode contributing to the energy loss

Surprisingly localized


2-3 nm?
0.6 nm @ 11 eV
0.4 nm @ 15 eV

Atomic resolution?
STEM-VEELS SPECTRA AND MAPS -- GRAPHENE
NOT preservation of elastic contrast

HAADF

HAADF at optimum focus

Zero loss

Bright field shows reverse contrast
Definition of Plasmons


\[
\text{Im} \left( -\frac{1}{\epsilon(\omega)} \right) \quad \epsilon(\omega) \rightarrow 0
\]

\[
\frac{\epsilon_2(\omega)}{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2}
\]

\[
\epsilon_1(\omega) = 0 \quad \epsilon_2(\omega) \approx 0
\]

J-C Idrobo
Plasmons in graphite

\[ \epsilon_1 (\omega) \]

\[ \epsilon_2 (\omega) \]

\[ \text{Im}[-1/\epsilon(\omega)] \]
“Plasmons” in graphene are interband transitions some of which are localized.

EELS simulation at atomic resolution

Dynamical Electron Scattering

\[ \psi(\mathbf{r}) = \sum_g \Psi_g e^{2\pi i (\mathbf{k} + \mathbf{g}) \cdot \mathbf{r}} \]

Density Functional Theory

\[ \psi = e^{2\pi i \mathbf{k} \cdot \mathbf{r}} \]

- NO SOLID STATE BONDING
- Detailed description of electron propagation (dynamical diffraction, channeling)
- Probe position dependence

- FULL SOLID STATE BONDING
- Incident electron is a plane wave—magically appears at the atom
- No incident beam direction
- No detector
- No spatial information

**Combining Electron Scattering & DFT**

![Core State to Final State Diagram](image)

\[ M_{if} (Q_g) = \left\langle \varphi_i (r) \left| \exp (2\pi i Q_g \cdot r) \right| \varphi_f (r) \right\rangle \]

\[ Q_g = q + g = (k + g) - k' \quad \text{momentum transfer} \]

**We measure intensities:**

\[ \left| M_{if} (Q_g) \right|^2 = M_{if} (Q_g) M_{if}^* (Q_h) \]

**Mixed Dynamical Form Factor (MDFF) – needed for STEM probe**

\[ S^{i,f} (Q_g, Q_h, E_{loss}) = \left\langle i \left| \exp (2\pi i Q_g \cdot r) \right| f \right\rangle \left\langle f \left| \exp (-2\pi i Q_h \cdot r') \right| i \right\rangle \]

**Dynamical Form Factor (DFF) – only applies for plane wave**

\[ S^{i,f} (q, E_{loss}) = \left| \left\langle i \left| \exp (2\pi i q \cdot r) \right| f \right\rangle \right|^2 \]
EELS: Inelastic Scattering Potential

The full inelastic scattering potential:

\[ W^{i,f}(r, r', E_{\text{loss}}) \propto \sum_{h,g} \mu^{i,f}_{h,g} e^{-2\pi i g \cdot r} e^{2\pi i h \cdot r'} \]

\[ \text{DFF} \Rightarrow \mu^{i,f}_{0,0} \propto \int_{\text{detector}} k' \frac{\left| i \exp(2\pi i q \cdot r) \right|^2}{|q|^4} d\Omega_{k'} \]

Mean value of the inelastic potential
The Inelastic STEM Image

The inelastic image as a function of probe position $R$.

$$I^{i,f}(R,t) \propto \int \sum_{h,g} \Psi_h^*(R,r'_\perp,z)\Psi_g(R,r_\perp,z)\mu_{h,g}^{i,f}dz$$

$$\text{DFF} \Rightarrow \mu_{0,0}^{i,f} \Rightarrow I \propto |\Psi_0|^2 \mu_{0,0}^{i,f}$$

The DFF contains no information about the probe position or propagation
For a given transition, fine structure will not change shape, only intensity
Near Edge Structure as a Function of Probe Position: O1 signal in LMO

Fine structure varies with probe position – need full simulation
Near Edge Structure as a Function of Energy: O1 signal

- Fine structure varies with energy
- Delocalization changes for transitions < 5 eV apart
- DFF or simple $d_{50}$ type expressions fail
- Need full simulation
THEORETICAL VEELS SPECTRA AND MAPS -- GRAPHENE

+1% noise

COMBINES DFT EXCITATION MATRIX ELEMENTS WITH DYNAMICAL SCATTERING
Experiment

+1% noise

a

b

c

d C=1.9 %

e C=4.1 %

f C=3.9 %
THE ATOMIC CHARACTER OF GRAPHENE STATES
SELECT ELECTRONIC EXCITATIONS AT $k = 0$

Images from states with maximum atomic character

- **non-dipole allowed**
  - $s - s$
  - $p_z - p_z$
  - $p_{xy} - p_{xy}$

- **dipole allowed**
  - $p_{xy} - s$
  - $p_z - d$
  - $s - p_{xy}$

Reverse contrast

- $C = 48.7\%$
- $C = 50.7\%$
- $C = 28.5\%$
- $C = 25.8\%$
- $C = 31.6\%$
- $C = 13.4\%$
THE ORIGIN OF GRAPHENE-LIKE IMAGES

All k points

![Graphene-like images with energy loss and number of excitations](image)

**Figure a:**
- Number of Excitations vs. Energy Loss (eV)
- Color codes:
  - $p_z \rightarrow p_z$
  - $p_{xy} \rightarrow p_{xy}$
  - $s \rightarrow s$

**Figure b-e:**
- Images with different energy losses and corresponding C values:
  - **b:** $E_{\text{Loss}} = 9 \pm 1$ eV, C = 6.1%
  - **c:** $E_{\text{Loss}} = 22 \pm 1$ eV, C = 3.9%
  - **d:** $E_{\text{Loss}} = 30 \pm 1$ eV, C = 5.6%
  - **e:** $E_{\text{Loss}} = 50 \pm 1$ eV, C = 5.4%
PROPOSED APPLICATIONS

• THEORY: DEMONSTRATE THE POWER OF ATOMICALLY-RESOLVED VEELS

• POINT DEFECTS

• INTERFACES

• MAGNETIC DICHROISM

• EXPT: NEED BETTER S/N RATIO AND ENERGY RESOLUTION
Bilayer graphene: oriented BLG

Tilt: 0°
Boundaries show dark

Width ~10 nm

Junhao Lin

Sok Pantelides
STEM images of Twisted Bilayer Graphene

Scale bars are 1 nm
EEL spectra of BLG (350 meV energy)

Experiments @ ORNL
EEL spectra of BLG (60 meV energy resolution)

Normalized EELS intensity vs. Energy Loss (eV)

- Optical change is continuous
- Incommensurability is NOT important

Experiments @ ASU
Dynamics of point defects...

Ce in AlN

R. Ishikawa and A. R. Lupini
UltraSTEM200
We can see atomic diffusion...

Ce in AlN

R. Ishikawa and A. R. Lupini
UltraSTEM200
Correlated vacancy-dopant motion
Interstitial “Kick-out” mechanism

Ce atom at interstitial sites

Simulate higher-temperature diffusion events!
Interstitial “Kick-out” mechanism

Kick-out mechanism

\[ X_{s} + I \rightleftharpoons X_{i} \]

- \( X_{s} \) : Substitutional dopant
- \( X_{i} \) : Interstitial dopant
- \( I \) : Self-interstitial

Simulate higher-temperature diffusion events!

Barrier : 3.7 eV
Why is the Ce barrier so low?

Large Ce atom is highly strained in a small AlN lattice
“I would like to try and impress upon you while I am talking about all of these things on a small scale, the importance of improving the electron microscope by a hundred times. It is not impossible; it is not against the laws of diffraction of the electron.”

Feynman’s goal = 0.1Å!“just look at the thing!”

STEM achieves 0.5 Å resolution

5th order aberration correction, 300 kV

Erni, R. et al., *Phys Rev Lett* 2009, 102, 96101; TEAM project

Sawada, H. et al., *J Electron Microsc* 2009, 58, 357; CREST project
But depth resolution is still on the \textit{nm}-scale

\begin{align*}
  d_{x,y} &= 0.61 \frac{\lambda}{\theta} \\
  d_z &= 2 \frac{\lambda}{\theta^2}
\end{align*}

30 mrad: few nm @ 300 kV
100 mrad: 4 Å @ 300 kV

Sub-unit cell resolution?

Need higher opening angles!
Depth resolution at unit cell level...

-10 nm

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Acceptance Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 kV</td>
<td>30 mrad</td>
</tr>
<tr>
<td>300 kV</td>
<td>60 mrad</td>
</tr>
<tr>
<td>300 kV</td>
<td>100 mrad</td>
</tr>
</tbody>
</table>

DEFOCUS

-10 nm

Normalized probe intensity

Depth of field

2 nm
Resolution in the 3rd dimension?

Tomography requires direct projection eg HAADF at low resolution.

At high resolution direct projection breaks down. Stability?

Natural transition to depth sectioning.
Substitutional Ce dopants in AlN

Ce @ 2.2 & 7.8 nm depth

defocus (nm)

0 1 2 3 4 5 6 7 8 9 10 11

30 mrad

60 mrad

100 mrad

Simulation by Ryo Ishikawa

thickness = 12.4 nm
No need to align the sample!

3D atomic structure!
We could look at glasses!

3D atomic structure!
We could see grain boundaries in polycrystalline materials!

3D atomic structure!
There’s still plenty to see at the bottom!

• Next generation corrector
  – 300 kV, CFEG, 60-100 mrad probe angle
  – ~0.2-0.12 Å diffraction limit

• Improved signal to noise ratio

• Optical properties with atomic sensitivity

• Improved precision of atomic positions

• 3D atomic resolution