Beating the Diffraction limit by 1000X
An introduction to nanoscale IR imaging on Bruker AFMs with applications in graphene

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Outline

- IR nanoimaging
- Results contributed by customers
  - First sSNOM data on Boron Nitride nanotubes
  - First sSNOM data obtained at ALS
- Results from Bruker Nano
  - First nanoscale IR images of Graphene’s Universal Conductivity
  - Fastest images yet of a nanoplasmon
Why do people use Infrared Spectroscopy?

Main reason: it allows chemical identification

Example IR spectrum

Absorption resonances = Unique IR fingerprint

Why Infrared sSNOM at the Nanoscale?
Characterization and Identification

**Polymers**

M. Raschke et. al. ChemPhysChem 2005

**Semiconductors**


**Biology: Tobacco Mosaic Virus**

M. Brehm et. al. NanoLett 2006

**Biology: Human Tooth Dentin**

G.O. Andreev – 2011, unpublished
Why Infrared sSNOM at the Nanoscale?
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Just how big is a 1000X improvement in resolution?

- **Far field IR image**
  - Grass
  - Ball
  - Paint
  - IR can ID main features of the soccer field
  - Resolution is limited

- **Near field IR image**
  - Soil compound
  - Stitching material
  - 1000X zoom
  - Nanoscale IR can ID the most subtle features
  - Resolution is 1000X better

*To make this transition we need to beat the diffraction limit*
Resolution limit in Far field optics

Far field imaging system:

We sample the object using plane waves:

\[
\frac{2\pi}{\lambda} = \sqrt{k_{||}^2 + k_{\perp}^2}
\]

\[
k_{||,max} = \frac{2\pi \sin \theta}{\lambda}
\]

\[
d_{min} = \frac{\lambda}{2\sin \theta}
\]

Far field optics limits IR resolution to \( \lambda \), or several \( \mu m \)
Resolution limit in near field optics

Near field imaging system:

We sample the object using many \textit{evanescent} waves

\begin{align*}
    e^{+ik_{\parallel}x} & \quad e^{-ik_{\parallel}x} \\
    + \text{ all possible } k_{\parallel}
\end{align*}

In the near field, $a \ll \lambda$

Now have access to imaginary $k_{\perp}$!

\begin{align*}
    2\pi/\lambda &= \sqrt{k_{\parallel}^2 + k_{\perp}^2} \\
    \text{Largest } k_{\parallel} &\gg 2\pi/\lambda \\
    k_{\perp} &\sim ik_{\parallel}
\end{align*}

For near field optics, resolution is limited only by distance to source

\begin{align*}
    k_{\parallel,\text{max}} &\sim 2\pi/a \\
    d_{\text{min}} &\sim a/2
\end{align*}
How do we create such a point source?

We use **sSNOM**: scattering Scanning Near-field Optical Microscopy

- Shining IR light on AFM tip polarizes the apex (Lightning rod effect)
- The apex turns into an IR point source ~ 10nm away from surface (tip radius)
- Detection: scattered light transfers near field info to far field

**Tip radius determines IR resolution = 10nm resolution**
Optical contrast in sSNOM for 3D and 2D materials: it works for both!

### 3D
- **Sample:** Insulating, Conducting, Resonant
- **Effect of sample:** $p_t$, $p_t^+$
- **Larger Reflection**

### 2D
- **Sample:** Non-resonant, Resonant
- **Effect of sample:** $p_t$, $p_t^+$
- **Larger Reflection**
Experimental Implementation
How the near field light ($E_{nf}$) is detected: Background Suppression and Interferometric Detection

Detector Voltage: $V_{det} \propto EE^* = |E_{ref} + E_{nf} + E_{bg}|^2$

Goals of the detection scheme:
1. Suppress the background, $E_{bg}$, contributions to detector voltage $V_{det}$
2. Perform a phase sensitive measurement of $E_{nf}$
How the near field light ($E_{nf}$) is detected: Background Suppression and Interferometric Detection

Detector Voltage: \[ V_{det} \propto |EE^*| = |E_{ref} + E_{nf} + E_{bg}|^2 \]

\[ \propto E_{ref}E_{nf} \cos(\varphi_{ref} - \varphi_{nf}) + E_{bg}E_{nf} \cos(\varphi_{bg} - \varphi_{nf}) + E_{ref}E_{bg} \cos(\varphi_{ref} - \varphi_{bg}) \]

Desired term

Suppressed terms: \[ + |E_{ref}|^2 + |E_{nf}|^2 + |E_{bg}|^2 \]

Tapping mode:

\[ E_{bg} \]

\[ E_{nf} + E_{bg} \]

$z > 50nm$

$z = 0 - 50nm$

sSNOM schematic:

MM = moving mirror
PM = parabolic mirror
BS = beam splitter
MCT = HgCdTe IR detector
sSNOM results from customers: implementation on Bruker AFM platforms
University of Colorado at Boulder
(Prof. Raschke Lab)

Parabolic Mirror

MCT IR Detector, Liquid nitrogen cooled

Piezo actuated mirror

IR Beamsplitter

XYZ stage

Parabolic Mirror, ~0.4NA effective

Bruker Innova*

*Innova Head removed to allow greater visibility of Parabolic Mirror
• Nanoscale intra-nanotube inhomogeneity revealed
• IR sSNOM spectra show contrasts over as little as 20nm
• Rich in information, beyond FTIR absorption

sSNOM results from Bruker Nano on a 2D material: Graphene
Introduction
Graphene Discovery, with Bruker AFM

- The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov (Univ. of Manchester)

"for groundbreaking experiments regarding the two-dimensional material graphene"

- Identification by optical survey (phase contrast) followed by AFM:

“AFM is currently the only method that allows definitive identification of single-layer crystals”
- Novoselov et al. PNAS 102 (30), 10451-3, 2005

Identifying single layers by AFM: (a) NbSe₂ and (b) Graphene. Novoselov et al. PNAS 102 (30), 10451-3, 2005
Introduction
What Is Graphene And Why Do We Care?

- **Graphene** = one-atom-thick sheet of (sp2-bonded) carbon atoms
  - Like 1 layer in graphite
  - 2D material = new class of materials

- **Lots of Superlatives:**
  - **Thinnest** material (1 atomic layer)
  - **Largest** surface area (2700sqm/g)
  - **Strongest** material ‘ever measured’ (theoretical limit)
  - **Stiffest** known material (stiffer than diamond)
  - Most **stretchable** material (20% elastically)
  - Record **thermal** conductivity (outperforming diamond)
  - Highest **current** density at RT (10^6 x Cu)
  - Completely **impermeable** (even to He)
  - Highest intrinsic **mobility** (100x Si)
  - Conducts **electricity** in the limit of no electrons
  - Lightest **charge** carriers (zero rest mass)
  - Longest **mean free path** at RT
Infrared study of Graphene: rich spectrum allows access to key observables

IR optical conductivity:

\[ 2E_f \pm \Gamma \]

Yields info about:

- **Carrier Density**
- **Defects**
- **Substrate Effects**
- etc…

sSNOM IR study of Graphene: same rich spectrum PLUS plasmonics

Near field spectrum yields same info as far field: Fermi energy, scattering rate
BUT also shows a plasmonic resonance – not present in far field
Let’s probe Graphene’s universal conductivity at the nanoscale
Bruker solutions for Graphene research:

TERS, colocalized Raman, PeakForce KPFM, QNM and now sSNOM
Colocalized SPM investigation of Graphene: Mechanical, Electrical, Optical

- **AFM**: layer heights, mechanical properties
- **Raman**: how many layers, defects
- **PF KPFM**: work function/Fermi energy
- **IR**: plasmonics, # of layers, Fermi energy

**Graphene Applications:**
- **AFM**: layer heights, mechanical properties
- **Raman**: how many layers, defects
- **PF KPFM**: work function/Fermi energy
- **IR**: plasmonics, # of layers, Fermi energy

**Images:**
- **AFM**: Confirmed n+1 layer
- **G-band Raman**: Confirmed 1,2,3,4 layers
- **D-band Raman**: ID defects, confirm n=1
- **IR 1730cm⁻¹**: Measure $\sigma(\omega)$
- **Upper Limit on $E_f$**: 80mV
sSNOM in universal conductivity regime: layer counting and unexpected results

• Expected: contrast consistent with Universal Conductivity
  - Confirmed $|\sigma_4| > |\sigma_3| > |\sigma_2| > |\sigma_1|$ for $\omega > 2E_f$
  - Reproducible – useful for layer counting

• Unexpected results:
  - $1L < \text{SiO}_2$
  - Huge jump from $3L$ to $4L$

Theoretical Prediction
sSNOM in universal conductivity regime:

Sensitivity to defects

Let’s zoom in..
Remarkable sensitivity: sSNOM images show fine contrasts due to defects

Nanomechanics shows signs of wrinkles

Hint of defects in D-band Raman

Easily detectable ~2% contrast
Now let’s switch to the plasmonic regime
sSNOM of Graphene in the Plasmonic Regime: launching and imaging

- Plasmon clearly observed in Single layer Graphene
- Origin: waves launched by tip reflecting back to tip
sSNOM of Graphene: fast imaging of plasmons

- 10Hz image obtained in just 60s
- No significant loss of spatial resolution

sSNOM on a Bruker AFM is fast without any loss in resolution
How important is the spatial frequency for Graphene plasmonics?

Dull Tip = low $k_{\parallel}$

Fresh Tip = large $k_{\parallel}$

$k_{\parallel, max} < k_{SP}$

$k_{\parallel, max} \sim k_{SP}$

Sharper tips have larger in-plane momenta – a necessity for plasmonics
Conclusion

- Near field imaging with sSNOM is powerful and unique
  - 10nm resolution – 1000X better than far field IR
  - Remarkable sensitivity to ultrathin materials
  - Access to nanoplasmonics

- New results
  - First nanoscale IR images of Graphene’s Universal Conductivity
  - Fastest images yet of a nanoplasmon

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