Nanoscale Measurement Methods for Novel Material Characterization

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Diblock Copolymers for Advanced Patterning

- Pitch and LER limit circuit density and device uniformity
- Diblock copolymers might help
- Significant optimization needed
- How do we measure their behavior?
Diblock Copolymers

Diblock Epitaxy
Variations in duty cycle, coverage and line-edge roughness

No variation in duty cycle, coverage and line-edge roughness
Sub-Lithographic Patterns

LER from SEM

ZEP

PS/PMMA

LER (nm)

0.37

0.40

0.43

0.45

duty cycle ($w_o/d$)

3.5 ± 0.3 nm

6.0 ± 0.6 nm

dose (μC/cm²)

950

1010

1070

1130

150 nm

150 nm
Resonant X-ray Scattering

Are interfaces sharp, chemically diffuse or rough?

- X-ray scattering can measure interfacial width or roughness to sub-0.5 nm accuracy.
- Different chemistries have distinct resonances.
- Resonant scattering enhances contrast from different chemical domains.
- C=C $\pi^*$ 285 eV, C=O $\pi^*$ 288 eV, C-O $\sigma^*$ 293 eV

Random Diblock Diffraction

$q_x (1/nm)$

$n=1$

$n=2$

$n=3$

200 nm

$\theta$ (deg)
Epitaxial Diblock Diffraction

\[ I_{q_x}^2 q_z^2 \text{ (a.u./nm}^4) \]

\[ 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \]

\[ q_x \ (1/\text{nm}) \]

\[ 1130 \mu \text{C/cm}^2 \]

\[ w_0/d = 0.45 \]
Interface Width from XRD

\[ \Delta^* = 2.33 \pm 0.13 \text{ nm} \]
Summary

- X-ray diffraction samples large areas
- Resonant scattering provides chemical contrast – diblocks, latent images, etc.
- Patterned nanostructure arrays yield lots of information
- Analysis relies on model
Solar Cells for Large-area Electronics

- Most work on material development, or device efficiency by trial and error
- Correlation of film morphology and charge transport not known
- Novel combined electrical and optical techniques needed
Organic PV Cell

- Donor and acceptor separate charge carriers
- Efficiency low in layered systems because of short exciton diffusion length
- Nanostructured blends reduce required length
Blended Organic Solar Cells

1:1 blend of Poly(3-hexylthiophene) (P3HT) to [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).
SPM Photocurrent Measurements

Photoresponse current measured with a conductive tip in contact mode while simultaneously mapping the surface topography.

532 nm laser focused into fiber optic cable

Signal at each pixel can be used to construct a 2D conductance map of the surface.
Most of these lack detailed quantitative analysis and a broad understanding. However, they have opened the door for a plethora of new problems to investigate!
Macroscopic Measurements

- Absorption and spectral response measure optical/electro-optical quality of PV films/devices.

UV-Vis for solution-processed P3HT:PCBM spun cast on glass. 500 nm: p-type polymer absorption (electron donor) 325 nm: n-type PCBM molecules.

Responsivity and (EQE) of OPV device with Al top contacts. EQEs of >50% in device absorption range comparable to the best reported to date.
Photocurrent vs Morphology

- 3-D topography overlaid with local short-circuit photocurrent measurements of blended P3HT:PCBM film
- Film prepared on top of TCO electrode modified by PEDOT:PSS.
- Darker regions correspond to substantial photocurrent collection.
Photocurrent vs Bias Voltage

- Short circuit condition: $V = 0$ V
- Reversed bias: $V = -0.3$ V
- Reversed bias: $V = -1$ V
- Forward bias: $V = +0.3$ V
- Forward bias: $V = +0.6$ V
- Forward bias: $V = +1.5$ V
Summary

- Photoconductive SPM is an important tool to study and characterize photovoltaic response of at the nm scale.
- Demonstrated measurements with new results on a well-studied material system
- Continue to add new imaging modalities
Graphene for Post-CMOS Electronics

- CMOS approaching scaling limits
- Graphene more amenable to large-area integration than CNTs
- Measurements of basic materials and device properties needed
Graphene Production Methods

  - Single device process
  - Wafer scalable process

Courtesy of Suyoung Jung, NIST

Courtesy of Walt de Heer, GT
Epitaxial Graphene on C-face SiC

- Multilayers on C-face are electronically decoupled

**Induction Furnace Method**

C-Face termination

SiC

Si-Face termination

J. Hass et al., PRL 100, 1255504 (2008)
Berger et al., Science 312, 1191 (2006)
STM Measurement of Quantization

- Direct measurement of density of states with scanning tunneling spectroscopy

- Spatial LDOS mapping

- Probe the $dl/dV(B,E)$ plane $dI / dV \propto \text{LDOS}$
Graphene Magnetic Quantization

- Hallmark of Graphene is the new Landau level quantization and \( \frac{1}{2} \) integer QHE – LLs have unequal spacing, special \( n=0 \) level

Graphene Landau level spacing

\[
\Delta E \approx 1000 \text{ K@10 T}
\]

“Standard” Landau level spacing

\[
\Delta E \approx 10 \text{ K@10 T}
\]

\( E_n = \text{sgn}(n)\sqrt{2e\hbar^2 |n| B} \)

Relativistic:

\[
E_n = E_\pm \pm \frac{\hbar e}{m^*} B(n+1/2)
\]

Standard Model:
Graphene Landau Quantization

- Direct measurement of graphene quantization
- Fixing $B$, sweeping $E$

- Quantization obeys graphene scaling
- Full quantization of DOS into Landau levels
- Very sharp LLs
- High mobility

Graphene quantization obeys the graphene scaling, leading to a full quantization of the density of states into Landau levels. The graph shows a plot of $dI/dV$ vs. sample bias, with peaks corresponding to Landau levels for different values of $n$. The graph is labeled with $B = 5$ T and indicates that the relaxation time $\tau \sim 0.4$ ps.
Tunneling Magneto-Conductance Oscillations (TMCO)

- High resolution $E-K$ dispersion from TMCO

$$E_F = (1.070 \pm 0.006) \times 10^6 \text{ ms}^{-1}$$
Origin of Electronic Decoupling

- STM Moiré patterns on c-face epitaxial graphene

![Images of STM Moiré patterns with dimensions: 20 nm, 3.8 nm, and 47 nm]
Landau Level Mapping

- Small potential variations in epitaxial graphene
Summary

- Epitaxial graphene on C-face SiC is a good candidate for carbon based electronics
- TMCO is a new STM measurement for high resolution low energy band structure
- Direct measurement of the new graphene quantization with tunneling spectroscopy
- Spatial mapping of LL offers great future potential to understand graphene physics
- See Miller, Kubista, Rutter et al. Science (in press) and www.cnst.nist.gov
Diblocks

- NIST
  - CNST
    - Alex Liddle
  - Postdoc
    - Gila Stein

Graphene

- NIST
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    - Kevin Kubista
    - Ming Ruan

- Univ. Texas Austin
  - Professors
    - Allan MacDonald
THANK YOU!
Backup Slides
Patterned Media for Hard Disks

Patterned media require:
Feature size < 20 nm
Size control < 2 nm, 3σ
Short-range placement < 2 nm, 3σ
Areas > 10 cm²

Beyond the limits of top-down nanopatterning

Pattern Noise

Diffraction picks up subtle variations across large areas
Resist Profiles
NEXAFS Data

Intensity (a.u.)

Energy (eV)

$t_0$

$t_f$

calculated
Sidewall Angle

![Graph showing sidewall angle as a function of duty cycle and dose. The graph displays data points for ZEP and PS-PMMA with error bars, and a trend line indicating a decrease in sidewall angle with increasing dose. The graph includes a note indicating a trend with a 3.4 ± 0.3° angle.](image-url)
Graphene Production Methods


Epitaxial Graphene on SiC

C-Face termination

(0001)

SiC

Si-Face termination

(0001)

Graphene layers

n~10^{10}/cm^2

n~10^{12}/cm^2

SiC
Epitaxial Graphene on Si-face SiC

- C-Face termination
- Si-Face termination

Our previous work on UHV grown Si-face material
- AB Bernal stacked epitaxial graphene
Previous STS Measurements on Graphite Surfaces

- Complex spectra
- Mixture of peaks of linear and non-linear in $B$

T. Matsui et al. PRL (2005)  
G. Li and E. Andrei  
Graphene Landau Quantization

- Multilayer epitaxial graphene on SiC is "graphene"!

\[ E_n = \text{sgn}(n)\tilde{c}\sqrt{2e\hbar B |n|}, \quad n = \ldots -2, -1, 0, 1, 2, \ldots \]
Origin of Electronic Decoupling

- Layer stacking

Alternating between: \textit{NEAR 30^\circ} \& \textit{NEAR 0^\circ}

Origin of Electronic Decoupling

- Rotated layers – STM Moiré patterns
Rotational Domain Boundaries

- Atomically flat and continuous across boundary

400 nm

50 pm
Rotational Domain Boundaries

20 nm 8 nm
Graphene Landau Quantization

- Complete field scaling of graphene quantization

\[ E_n = \text{sgn}(n) \tilde{c} \sqrt{2e\hbar B |n|}, \quad n = \ldots -2, -1, 0, 1, 2, \ldots \]
Magnetic Quantization

- **Cyclotron motion in a magnetic field**
  - Quantized orbits and energy levels
    \[ E_n = \frac{\hbar e B}{m^*} (n + 1/2) \quad n \geq 0 \]  
    Standard 2DEG
    \[ E_n = \text{sgn}(n) \sqrt{2e\hbar c^2} |n| B \quad n=0, \pm 1... \]  
    Graphene

- **Magneto-oscillations**
  - De Haas-van Alphen and Shubnikov-de Hass effects; oscillations in physical properties due to quantization of density of states
  - Tunneling magneto-conductance oscillations
Tunneling Magneto-Conductance Oscillations (TMCO)

- Fixing $E$ and sweeping $B$

Analogous to Shubnikov-de Haas oscillations but with one big difference

$$B = \left( \frac{\hbar}{2\pi e} \right) A_F \quad A_F \rightarrow A_E$$

Low energy band structure to be measured with high energy and momentum resolution
Origin of Electronic Decoupling

- Rotated layers with Preferred Domains - LEED

- SiC bulk
- Graphene

Surface X-ray Diffraction

- C-Face
- RF furnace grown
- 72.2eV

Graphene
- R±2.2
- R30

Joanna Hass et al. PRL 100, 125504 (2008)
Origin of Electronic Decoupling

- Rotated bilayer maintains linear dispersion

F. Varchon and L. Magaud, CNRS

Graphene bilayer
Isolated graphene sheet
R30/R2 fault pair
Tunneling Magneto-Conductance Oscillations (TMCO)

- Fan plot; Landau index $n$ vs. $1/B$

Slope of $n$ vs. $1/B$ determines $B_E$

\[
B_E = \left(\frac{\hbar}{2\pi e}\right) A_E
\]

Circular energy contours at $E=V_B$

\[
A_E = \pi k_E^2
\]

\[
k_E = \left(\left(\frac{4\pi e}{\hbar}B_E\right)^{1/2}
\right)
\]