NEXAFS Microscopy and Soft X-Ray Resonant Scattering

Workshop: "Unique Opportunities in Soft Materials and Nanoscience with an ERL"

Cornell, June 19, 2006

H. Ade
Department of Physics
North Carolina State University
http://www.physics.ncsu.edu/stxm/

Thanks to J. Stoehr, G. Mitchell for their viewgraphs/data and many other colleagues, collaborators, and users

Thanks to organizers for the invitation and support and NSF, DOE, Dow Chemical for financial support over the years
Motivation and needs

Soft matter = lots of carbon!
Microscopy:
Structure characterization in real space

Early Microscope
Scattering/diffraction: Structure characterization in reciprocal space

Small Angle Scattering
Coherence length larger than domains, but smaller than illuminated area

Spallation Neutron Source: total cost of $1.4 billion, http://www.sns.gov/

Structure function: information about domain statistics.
X-ray Microscopy has come a long way!
(Examples “biased” towards spectromicroscopy/polymers/magnetic materials. – No bio or cryo)

NEXAFS microscopy (STXM) 1992
XMCD microscopy (PEEM) 1993

XLD microscopy (STXM) 1993
XMCD microscopy (TXM) 1996

Dynamics (PEEM)

Still a long way to go before we hit fundamental limit!!!
First NEXAFS imaging in transmission (1992)
polypropylene/styrene-acrylonitrile

- Based on the Stony Brook X1A-STXM (1989-present)

- Stony Brook-STXM not explicitly built to perform spectroscopy, but proved flexible enough to perform carbon NEXAFS.
  - Polymer Science was “enabled”

\[ \pi^* \text{ of styrene (C=C, 285.5 eV)} \]
\[ \pi^* \text{ of acrylonitrile (286.8 eV)} \]
\[ \sigma^* \text{ C-H (287.9 eV)} \]

Data: Stony Brook STXM at NSLS
X-Linear Dichroism Microscopy

Kevlar 149 fibers, 200 nm thick, imaged at 285.5 eV

- Pattern rotates with rotation of polarization due to radial orientation of phenyl groups
- Phenyl and carbonyl groups point (on average) radially outward
- $\pi^*$ and $\sigma^*$ resonances show complementary dichroism
- Degree of orientation of various fiber grades can be quantified


Determine degree of orientational order

Spectra with horizontal polarization in locations indicated


Data: Stony Brook STXM
Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Example: “”Richness” of Polymer NEXAFS Spectra

Unoccupied Molecular Orbital

Unsaturation C=C

Unsaturation C=O

C 1s edge ~ 290 eV
N 1s edge ~ 405 eV
O 1s edge ~ 540 eV
Some Polymer NEXAFS Spectra

Dhez, Ade, and Urquhart

Data: Stony Brook STXM at NSLS
Basis for Resonant Scattering Contrast: Carbon edge examples

Scattering factors $f'$ and $f''$ (optical const. $\delta$ and $\beta$, respectively) show strong energy dependence.

Absorption (NEXAFS)

```
  0.005
   0.004
   0.003
   0.002
   0.001
   0.000
280   290   300   310
```

Dispersion

```
  0.002
  0.001
  0.000
-0.001
-0.002
-0.003
270   280   290   300   310
```

$I \propto \Delta \delta^2 + \Delta \beta^2$

- “Bond specific” scattering!
- Substantial potential as complementary tool!
PMMA/P(BA-co-S)

Idealized, “consensus” particle

“PS” “shell”

P(MA-b-MMA) / PS

Different process and composition
- Fuzzy TEM
- modified core/shell structure?
- Phase less separated?
- Where really is the PS?

“PS” effective radius larger than PMMA “radius”

First results from structured polymer samples
Some Polymer NEXAFS Spectra

Lots of contrast from β and hence δ (Kramers-Kronig), for I ∝ Δ δ^2 + Δ β^2

marry spectroscopy with structure from scattering

Reduced need to deuterate!

Data: Stony Brook STXM at NSLS
Low Contrast Example: Developmental Porous SiLK* Resins
G. Mitchell, Dow Chemical

- Decreasing feature size in integrated circuits require lower dielectric constants for insulating layers to:
  - increase circuit speed, decrease power consumption, decrease crosstalk
- Adding pores to SiLK dielectric resin is used to decrease dielectric constant from 2.65 to 2.1 and less
- Future materials require more and smaller pores


* SiLK is a trademark of The Dow Chemical Company
Systematic variation in porogen size

Wouldn’t be able to do the experiment with STXM, TEM, or SAXS. - Deuteration and SANS would work.

Data: Beamline 6.3.2 ALS

H. Ade et al., ERL 2006
Soft X-ray Resonant Reflectivity

PS/PMMA bilayer

C. Wang, T. Araki, H. Ade

- Observed strong photon energy dependence
- Need to reduce uncertainty for \( \delta \) and \( \beta \)

Potential: Diffuse scattering from interfaces

Complementary Tool to Neutrons and hard X-rays

Data: Araki, BL6.3.2. ALS, Berkeley

H. Ade et al., ERL 2006
NEXAFS microscopy and Resonant Scattering

- Unique tools for soft condensed (carbonaceous) matter
Brighter Sources!
How do we take advantage of them? Space, time, energy?

How about my favorite absorption edge??
Carbon, 300 eV?
Types of X-ray Microscopes

**X-Photoemission Electron Microscope (PEEM)**
- X-ray Beam
- Sample
- Aperture
- Objective Lens
- Projective Lens
- Magnified Image
- MCP
- Screen

**Conventional X-ray Microscope XM-1 at the ALS (TXM)**
- ALS Bending Magnet
- Plane mirror
- Condenser zone plate
- Micro zone plate
- Sample stage
- Fast
- Limited NEXAFS

See talk by Maya Kiskinova for details
Zone Plates: Diffractive Optics for X-rays
Developed by groups in Goettingen/Bessy, LBNL, Stony Brook/Lucent, a few others

  - 1978: Move to ACO
  - 1982: Move to BESSY-I
- 1982: First STXM at NSLS: Rarback and Kirz
  - 120 nm resolution

Arrangement in a Scanning Transmission X-ray Microscope (STXM)

- Circular Au, Ni, or Ge structures
- Nanofabrication with E-beam lithography
- Spatial resolution equal approx. outermost zone width
- Focal length is proportional to energy

- Diameter: 150-250 μm
- Zone widths presently as small as 15 nm
- Working distance: ~150 μm

**Recent STXM Technology Innovations:**

1) Interferometer, 2) polarization control

### 5.3.2 Polymer STXM, Fall 2001, “35 nm zone plate”

Soon to install “25 nm zone plate”

### BL11.0.2.2 STXM, Spring 2004, “25 nm zone plate”

New 25 nm CXRO zone plate test:
25 nm lines of a test pattern obtained at 395 eV.
* Polarization control

**Impact:**
1) Zone plate are now the spatial resolution limiting factor,
2) enables magnetism,
3) quantification, wider range of samples

---

TXM: ALS Beamline 6.1.2 XM-1
Spatial resolution record

15 nm zone width, 1.7 nm placement accuracy

How do we get to <10 nm resolution?

- **Volume zone plate very difficult to make**
- **Aspect ratio for low efficiency zone plates is easier to achieve**
- **ERL eliminates need for high efficiency zone plates**
  - Low efficiency is compensated for by increased brightness
- **Alternative: Use third order: 1/9th the efficiency, 3x better spatial resolution**

**Volume zone plates with tilted structures**

Gerd Schneider, BESSY, Berlin

**diffraction efficiency $\eta_1(\text{d}r_n)$**

- 200 nm Ni
- 520 eV

**Thin ZP plates**

Au Density=19.32, Alpha=0.5, Thickness=20 nm

http://www-cxro.lbl.gov/optical_constants/tgrat2.html

---

H. Ade et al., ERL 2006
Instrument challenges for STXM

Relative ZP/sample vibrations (5.3.2 STXM)

Image-sequence alignment

- Auto-correlate images to detect shifts
  - Random shifts less than 30 nm
  - Some residual misalignment in y
Time resolution real space: STXM

- Recall: Mechanical scan of sample or optics
- “Scan speeds” presently as low as 100 μs/20 nm pixel
- 1000x1000 pixel image in 2 minutes

- Difficult to imagine technology that can really take advantage of ERL for imaging speed alone
  - Pump probe on radiation hard materials (e.g. magnetic materials) in STXM and PEEM
Sine excitation @ STXM

H. Stoll et al. MPI, Stuttgart
(sample prep.: I. Neudecker, D. Weiss, C.H. Back, Regensburg Univ.)

Permalloy sample A
(1.5 x 1.5) μm², 50 nm thick

\[ B_0 \approx 16 \text{ mT} \]
\[ f = 250 \text{ MHz} \]

\[ B_0 \approx 10 \text{ mT} \]
\[ f = 250 \text{ MHz} \]

\[ B = B_0 \sin (2\pi ft) \]

Change of vortex core chirality (handedness)
Use ERL for improved energy resolution?

- NEXAFS already limited by core-hole lifetime
- Resonant Inelastic X-ray Scattering for improved spectroscopy
  - But, damage!
  - Need to back off on spatial resolution
Radiation Damage

- Typical critical dose $\sim 1000 \text{ eV/nm}^3$
- Rose criterion for detection: $S/N=5$
- Transmission, $S=-\ln(I/I_0)$
- $(10 \text{ nm})^3$ PS feature has $S/N$ of 5 for 650 incident photons, and 115 absorbed photons in $\pi*$ peak at 285 eV
  - Dose $\sim 32 \text{ eV/nm}^3$
- Quantitation/spectra/tomography typically require 100x dose
  - Near critical at 10 nm for PS
  - Dose $\propto 1/(\Delta \alpha)$

- Imaging using phase contrast
- Scattering using phase and absorption contrast

What about scattering?

- $I \propto \Delta \delta^2 + \Delta \beta^2$
  - Works with low contrast
- Q-range $\sim 3 \text{ nm}^{-1}$ (@300 eV)
- Dose is distributed!!
- Time resolution could be quite good
- “SAXS” not intrinsically a brightness driven experiment
- Combine low resolution STXM and SAXS: Microbeam scattering
  - Damage?
“Incoherent“ vs. Coherent X-Ray Scattering

Small Angle Scattering
Coherence length larger than domains, but smaller than illuminated area

Speckle
Coherence length larger than illuminated area

Figure courtesy J. Stohr

Resonant scattering and resonant coherent speckle/imaging should be excellent tools for many materials!
New tools
(Jan Luning’s talk)

Technique of choice for use at ERLs
damage limit?

Phase problem can be solved by “oversampling” speckle image

Transmission X-ray Microscope

“Reconstruction” from Speckle Intensities

Figure courtesy J. Stohr


Conclusions

- NEXAFS imaging, Resonant Scattering
  - High, tunable contrast: Compositional, i.e. “bond specific” sensitivity
- Technology: STXM, PEEM, SPEM, scattering, speckle
  - Good progress over the last 20 years
  - These techniques will benefit greatly from new sources, more capacity, more competition, better zone plates
- New zone plate optics strategy
  - STXM with spatial resolution < 10 nm possible, but challenging
- Higher energy offer relatively larger payoff (coherent volume $\propto \lambda^2$)
- Radiation damage a limitation in absorption mode
- Microbeam scattering
- Resonant coherent imaging in phase mode is good idea (Jan Luning’s talk?)
  - Resonant photon correlation spectroscopy
- Pump probe experiments will have better time resolution
Thank you for your attention!!!!

Post Doc hire by this fall
Resonant scattering/reflectivity: Conclusions

- High, tunable contrast
- Compositional, i.e. bond specific, sensitivity
- Multiple modes: Scattering and reflectivity

- Soft X-ray should be good complement to neutrons and hard x-rays
- Good complement to TEM, SPM, STXM, SANS/SAXS
  - Reality check!???

Future:
- Contrast from orientation!
- Control of sample environment
- Resonant coherent imaging?

NEXAFS microscopy sensitive to orientation
Reflectivity at the PS/PMMA interface is related to the contrast between PS and PMMA

$$R_{12} = r_{12}^2 \approx \left| \frac{(\delta_2 - \delta_1) + i(\beta_2 - \beta_1)}{(1 - \delta_1 - i\beta_1) + (1 - \delta_2 - i\beta_2)} \right|^2 \approx \frac{\Delta\delta^2 + \Delta\beta^2}{4}$$

Rapid changes as the function of photon energy.

Can use large angles, hence, get good q-range

• At 280, 285.2eV, 288.8eV —— bilayer signature
• 283.2eV —— only single PMMA layer
• 320 eV and 8 keV —— essentially only full layer signal
PS/PMMA interface: hPS and dPS

dPS/PMMA has larger interface than hPS/PMMA
- Implications for neutron work, comparison to theory, capillary waves, etc.
Direct comparison to Neutron Reflectivity

<table>
<thead>
<tr>
<th>Method</th>
<th>Bilayers</th>
<th>D (nm) dPS</th>
<th>D (nm) PMMA</th>
<th>$\sigma_{\text{rms}}$ (nm) dPS/Air</th>
<th>$\sigma_{\text{rms}}$ (nm) dPS/PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>RXR</td>
<td>dPS(50nm)/PMMA(200nm)</td>
<td>43.3</td>
<td>187.3</td>
<td>0.55</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>dPS(100nm)/PMMA(200nm)</td>
<td>98.5</td>
<td>189.3</td>
<td>0.77</td>
<td>1.48</td>
</tr>
<tr>
<td>Neutron Reflectivity</td>
<td>dPS(50nm)/PMMA(200nm)</td>
<td>41.7</td>
<td>188.8</td>
<td>0.43</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>dPS(100nm)/PMMA(200nm)</td>
<td>96.5</td>
<td>190.3</td>
<td>0.49</td>
<td>1.46</td>
</tr>
</tbody>
</table>

$\sigma_{\text{rms}}$ hPS/PMMA = 1.16 nm
Conclusions

Opportunities

- **Technology:** STXM, PEEM, SPEM, scattering, speckle
  - Tremendous progress over the last 20 years
  - Clearly all these techniques will benefit greatly from new sources, more capacity, more competition, better zone plates

  and most importantly new and exited users

- **Science**
  - Polymers! - Yes, but radiation damage might set a limit
    - Polymer-inorganic bybrids
    - Templating

  - Magnetic materials
  - Nanoscience in general
  - Biology