A NOVEL LARGE AREA IMAGING NEXAFS SPECTROMETER FOR COMBINATORIAL CHEMICAL AND STRUCTURAL ANALYSIS

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LARIAT NEXAFS Imaging Spectrometer

Where Does It Live?

Synchrotron Methods and Measurements

Current home of LARIAT MKI
NSLS I
BNL
Beamline U7A
(commissioned July 2008)

Future home of LARIAT MK II
NSLS II
BNL
(2012-2013)
Synchrotron Methods and Measurements

Retractable Wobble Mirror optics for creating tunable Soft X-ray beam - 13 mm x 18 mm areas (2 Beam Paths)

Automated manipulator system and sample introduction
Gradients or Sample Array (100s samples)

Pass Through to next Experimental Chamber

Large Area Magnetic Imaging Electron Energy Analyzer
Parallel process NEXAFS imaging
13 mm x 18 mm areas with 75-micron spatial resolution

New automated endstation for full field NEXAFS imaging (parallel process)
LARIAT NEXAFS Imaging Spectrometer
Brookhaven National Laboratory
Beamline U7A
Spectrometer Overview
LARIAT NEXAFS Imaging Spectrometer: Principle of Operation

NIST SBIR Phase II Awarded to E. L. Principe & Assoc. (Imaging NEXAFS detector)
“Large Area Imaging Two-Dimensional Electron Energy Analyzer”

Synchrotron Methods and Measurements

- Cyclotron Radius determines resolution*.

\[ CR_{\text{max}} = \frac{3.4 \times \sqrt{E_T}}{B} \]

For electron energies in electron volts where \( CR_{\text{max}} \) is in microns

\[ Mag = \sqrt{\frac{B_0}{B}} \approx 2 \]

Soft x-ray beam
15 mm x 20 mm

1 Tesla shaped pole

Sample rotation

High pass grid

- Diverging magnetic field converts transverse energy into energy along B field lines.
- If field decreases from \( B_0 \) to \( B \), transverse energy decreases from \( E_t \) to \( E_t(B/B_0) \)

\* To 1\textsuperscript{st} order
• Diverging magnetic field converts transverse energy into energy along $B$ field lines.
• If field decreases from $B_0$ to $B$, transverse energy decreases from $E_t$ to $E_t(B/B_0)$

* To 1st order
LARIAT NEXAFS Imaging Spectrometer: Detection System

MCP / Phosphor / Optical taper / CCD Camera

Synchrotron Methods and Measurements
LARIAT NEXAFS Imaging Spectrometer: Results
Spatial Resolution ~ 50 microns at high retarding grid bias

Electrons with axial energy below the grid potential are rejected

Carbon NEXAFS images
13.5 mm x 18 mm = 600x800
i.e. ~ 22.5 microns / pixel

Photoresist grid on Si
200 micron lines, 600 micron centers

Color image at 285 eV
High Throughput NEXAFS: Soft Matter Structure and Chemistry

Synchrotron Methods and Measurements

Near Edge X-ray Absorption Fine Structure (NEXAFS)  Soft X-rays 175 – 1300 eV

- Photon energy scanning
- Resonance/Final State/Orbital
- Electric field vector incidence
- Adjusting the Grid Voltage
- Elemental selectivity
- Chemical bond sensitivity
- Orientation Information
- Depth selectivity

Absorption Probability

Photon Energy

Measuring LUMO

Continuum States

Vacuum level

\( \pi^* \)

\( \sigma^* \)

285 eV

Carbon 1s

Auger Electron
(top 10 nm)

Fluorescent Photon
(top 200 nm)

Polarized soft x-rays

Carbon
Data is acquired as a series of images each at a single primary x-ray energy. And display as a linear combination of images... or extracted spectra.
"Regions of Interest" – aggregations of pixels used to define spectra can be defined in multiple ways including arbitrary polygons, squares of fixed size and positive or negative thresholds.

Threshold selection

**ROI**

Spectra can be extracted from areas as small as single pixels....

......or aggregated from multiple areas for improved S/N

Composite is sum of normalized images at energies 399.2 - 399.8 eV

LARIAT NEXAFS Imaging Spectrometer: Data Reduction

Hyperspectral Imaging Acquisition and Analysis Package

- Threshold selection
- ROI

**DNA-N-theta30-60s wROI: File Comment**

**Data Select**

**Raw Images**

**Image 1**

- **OP**:
  - Off
  - 
  - +
  - r/g
- **None** / **Pre-Edge** / **Pre-Post**

**Normalize**

**Composite is sum of normalized images at energies 399.2 - 399.8 eV**
Images are constructed from portions of the spectra to show spatial distribution of chemical information.
Reduces thousands of spectra to a few, with no loss of chemical information.

Uses information from all pixels to improve the spectral signal/noise.

No user bias or assumptions required for component identification*.

Rapidly finds the small, hidden features of the chemistry or microstructure.

*Other than non-negativity, linear additive model and Poisson noise characteristics

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

Tony Ohlhausen
Synchrotron Methods and Measurements

Nitrogen K edge NEXAFS 300 image stack
AXSIA Multivariate Analysis reduces to single image
Identify N chemistry in ssDNA chips
from N chemistry in substrate

Adenine $\pi^*$ N=C  Low Noise Spectra and Images
Organic bulk heterojunction Photo Voltaic improvements

Patterned SAM induces lateral PCBM segregation; P3HT skin found

Depth Contrast using retarding grid voltage - 3D imaging

Parallel process NEXAFS imaging of Soft Matter (13 mm x 18 mm areas)
SAM gradients, DNA / protein chips, Catalyst libraries, Patterned surfaces

Synchrotron Methods and Measurements

P3HT skin found “Shallow” (-200 V bias)

w/ U.W. (Ginger)

PCBM segregation (“Deep” - 50 V bias)

C-60 π* peak

circle stamp 300 μm dia.

electron acceptor

light absorber

stamp: acid
backfill: alcohol

(Dean Delongchamp NIST/MSEL/ Polymers Div.)
Characteristics of LARIAT NEXAFS Spectrometer

**Features**

- Magnetic projection electron imaging
  - Electrons follow B field lines to form parallel imaging system
  - Helical orbits $r = \frac{mv_{\text{perp}}}{qB}$
  - Nearly 100% Collection efficiency » (high throughput)
- Large depth of field
  - i.e, Curved surfaces
- Orientation images
  - (via sample rotation)
- High pass grid energy analyzer
  - Rejected electrons return to sample (plays role in sample neutralization)
  - Depth selectivity 3D imaging
  - Spatial resolution optimization
- ~725 images per hour
  - 800X600 pixels

**Benefits**

- Sensitivity, sensitivity, sensitivity.
- Ease-of-use. Easy to get images.
- No column tuning.
- Robust. Insensitive to mechanical tolerances. Insensitive to stray fields.
- No high voltages (except detector).
- Very wide bandwidths with no loss of sensitivity.
- No neutralizer.
- Image resolution constant across field.
- The sample can be rotated normal to the x-ray beam if desired.
- Simple electronics.
NIST SBIR Phase III Awarded to E. L. Principe & Assoc. (Imaging NEXAFS detector)
“LARIAT MKII Super Conducting NEXAFS Imaging Spectrometer”
ARRA Funding (NIST SB134109SU1067)

- 8T Sample Magnet
- 0.8T Detector Magnet

**Analytical Modeling**
- 5um spatial Resolution
- Two “grid less” ES elements
- 400mm² area
- 16Mp camera
- 1MHz Acquisition

**Numerical Methods Modeling**
LARIAT MK II Configuration: Axial Introduction

Zoom magnification is possible by Decreasing Detector B Field

~0.66T

~8.5T @ sample

CCD Detector

Low Field Retarding Element

High Field Retarding Element

Electron Trajectories

Sample
Analytical Modeling of LARIAT MK II

Cyclotron Radius distribution at sample

Sq root of energy matrix

\[ CR_{0, i,j} = \frac{3.38}{E_0} \cdot \text{sqr EE}_{i,j} \cdot \cos TT_{i,j} \]

Sample B Field

Angular Distribution Matrix

\[ II2TT_{i,j} = II2_{i,j} \cdot \sin \{ TT_{i,j} \} \cdot TMT0_{i,j} \cdot TMT1_{i,j} \]

Angular Intensity Distribution

Total Intensity

1st Retarding Element

2nd Retarding Element

\[ CRav = 1.37 \]

EO = 250
B0 = 8
Vg0 = 200
Bg1 = 1
Vg1 = 0
max(CR0) = 6.68
max(CR3) = 8.42

Intensity Distribution as a Function of Energy

Idealized Electron Distribution

Energy (eV)

High Field Retarding
Low Field Retarding

Cyclotron Radia
Parallel process NEXAFS imaging of Soft Matter (13 mm x 18 mm areas)
SAM gradients, DNA / protein chips, Catalyst libraries, Patterned surfaces

**Creating Orientation Images of SAM gradients**

Dichroic Ratio of C-F NEXAFS peaks derived from 20°, 55°, and 90° θ incidence NEXAFS image stacks

\[ 300 + 300 + 300 = 900 \text{ images!} \]

\~500,000 NEXAFS spectra / stack

C-F Dichroic Ratio = \( \frac{I_{90} - I_0}{I_{90} + I_0} \)

\[ 55° \text{ degree incidence (magic)} \]

C-F NEXAFS peak image

\[ 0.7 \]

J. Genzer and K. Efimenko
Parallel process NEXAFS imaging of Soft Matter (13 mm x 18 mm areas) SAM gradients, DNA / protein chips, Catalyst libraries, Patterned surfaces Synchrotron Methods and Measurements

Orientation (Dichroic) Image of SAM gradient

Orientation tracks Coverage

C-F Relative Intensity

C-F Dichroic Ratio

Distance (mm)

C-F Ratio (292.6eV Peak) Dichroic Ratio

0 2 4 6 8 10 12

-0.1 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7

10 mm
SUMMARY:

LARIAT - Large Area Rapid Imaging Analytical Tool
E.L. Principe & Associates, NIST SBIR Funded

- Bond Concentration and Orientation Images
  NEXAFS partial electron yield images

- High throughput, rapid full field imaging
  Large area 13 mm x 18 mm

- 50 micron spatial resolution, 5 micron coming

- Depth selectivity over a 10 nm range
  Possible 3D imaging

EXAMPLES
1. Semi-fluorinated SAM gradients
2. Single-strand DNA micro array sensors
   - AXSIA multivariate analysis (Sandia)
3. Organic electronic combinatorial device arrays
Some of our users since July 2008:

- **Dean** - organic electronics - photo voltaic -> device array, PV blends x3
- **Jan Genzer** - SAM gradients -> 1 and 2 dimensional gradients, different condition lots of samples
- **Castner** group - single strand DNA arrays, SAM arrays (mosaic x2), protein arrays
- **Carpick** (U Penn) - arrays of small spheres subjected to tribological wear
- **Sandia** - SAMs subjected to various troblogical treatments - some Tony test samples, twenty dollar bill - arrays of sputtered dots on an oxide sample
- **BNL Battery group** - array of Li ion batteries (2-3 mm) at various stages of charge and discharge - these are really neat!
- **BNL Diamond Group** - diamond sample subjected to laser abolation, an array of different laser power densities and times all laser spots in the array subjected to repeated UV ozone cleaning to remove graphite to clean the ablated laser spots.

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As well as users who gave permission to use their data!