Further Development of Soft X-ray Scanning Microscopy with an Elliptical Undulator at the Advanced Light Source

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Soft x-ray scanning microscopy (1) is under continuing development at the Advanced Light Source. Significant progress has been made implementing new scan control systems in both operational microscopes (2) and they now operate at beam lines 5.3.2 and 11.0.2 with interferometer servo scanning and stabilization. The interferometer servo loop registers the images on a universal x/y coordinate system and locks the x-ray spot on selected features for spectro-microscopic studies. At the present time zone plates are in use with 35nm outer zone width and the imaging spatial resolution is at the diffraction limit of these lenses. Current research programs are underway in areas of polymer chemistry, environmental chemistry and materials science.

A dedicated polymer STXM is in operation on a bend magnet beam line (4) and is the subject of a separate article (3) in this issue. Here we focus on the capabilities of STXM at a new beam line that employs an elliptical undulator (5) to give control of the polarization of the x-ray beam. This facility is in the process of commissioning and some results are available, other capabilities will be developed during the first half of 2003.

Beam Line Capabilities

Figure 1. Beamline 11.0.2 at the ALS. The monochromator is foil-wrapped at the lower left. The line branches by means of a movable mirror and each branch has its own set of exit slits. The STXM branch is seen here, with the STXM enclosure to the upper right.

Figure 1 shows the beam-line. A newly engineered entrance-slit-less SX700 monochromator operates in collimated light (6,7) and serves the microscope part-time. The new monochromator has been engineered to emphasize cooling and cleanliness. The flux reduction at the carbon edge is about 30%. Much of the research on this line will involve organic molecules, studied at the C1s absorption edge.

Figure 2 is the standard resolution test, measuring N_2 vibrational levels using a partial pressure of air in the microscope enclosure.
Figure 3 shows the computed count rates in the microscope, operating the monochromator with three different values of the focusing parameter
$C_{ff} = \cos\beta / \cos\alpha$

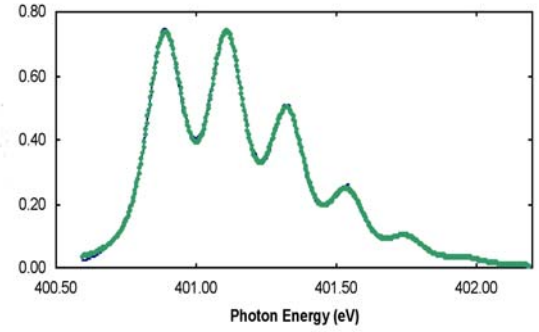

Figure 2. N_2 absorption spectrum, with a spectral resolving power of around 8000.

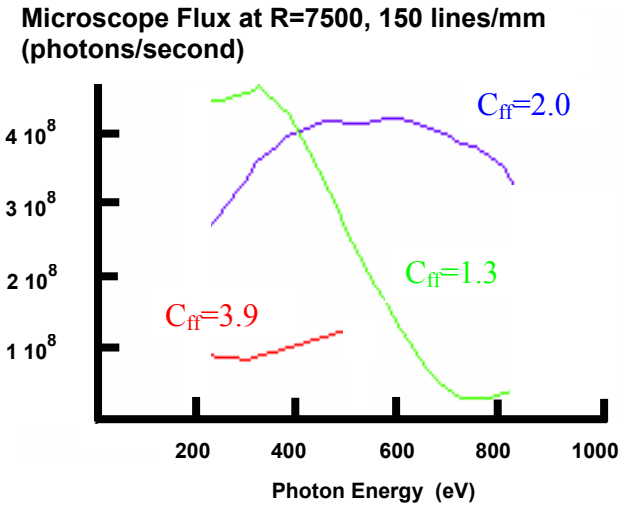

Figure 3. Computed microscope illumination.

C_{ff}=1.3 has higher diffraction efficiency and smaller dispersion for maximum count rate. C_{ff}=3.9 provides high spectral resolution with a large safety margin against vertical electron beam motion.

Microscope performance

At this time the microscope operates at room temperature in an enclosure that can be evacuated, or operated with a helium atmosphere. X-rays are focused by a zone plate with 155µm diameter with 35nm outer zones (8). The instrument operates with photon energy from 150eV to 2000eV. The detector is a phosphor-photomultiplier combination detecting transmitted photons with an efficiency between 5% and 50% Figure 4 shows the spatial resolution achieved with the microscope at the new beam line. In addition to the advantages of the interferometer servo system the new beam line offers higher count rates and lower intensity fluctuations, so that better quality images can be obtained at faster acquisition rates.

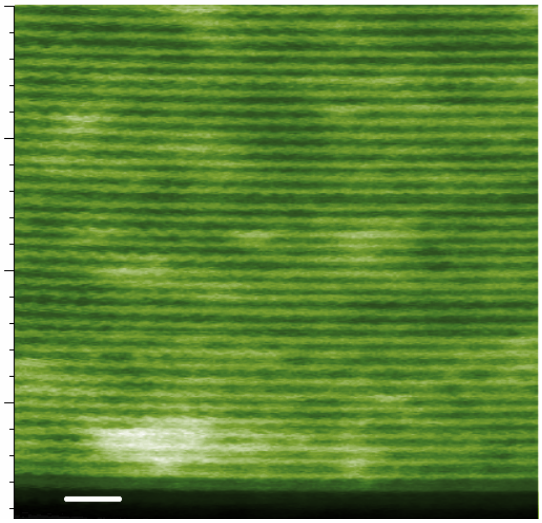

Figure 4. X-ray image of the outer zones of a zone plate with 25nm outer zone width. The bar in the figure is 200nm long. This image was acquired counting for 1ms per pixel at 390eV.

Linear Dichroism Microscopy of Semi-Crystalline Polymers

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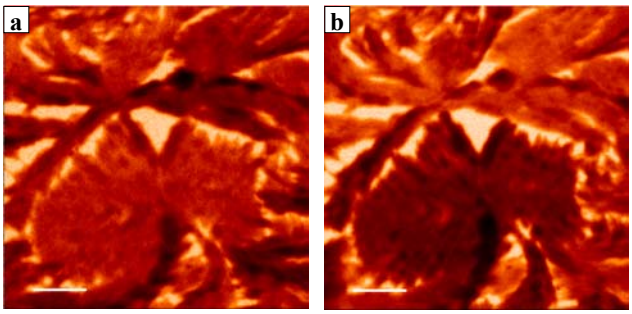

Fig. 5. Thin poly-ethylene film with spherulitic crystallites imaged at 288 eV with horizontal (left) and vertical (right) linearly polarized x-rays. (Scale bar = 5 μm).

Semi-crystalline polymers, including most thermoplastics, are a class of materials that are ubiquitous, yet various aspects of their properties including their crystallization behavior are still poorly understood. In thin films, due to the effects of the interfaces, the issues are compounded to the point that it is unclear to what degree the films crystallize and what orientation crystallites have. X-ray linear dichroism microscopy (9) is a potentially very powerful tool to address many open questions, but dichroism microscopy applications have been limited due to difficulties with image registration if samples are rotated. The elliptical undulator which illuminates the 11.0.2 STXM will eliminate these constraints. Complete control over the orientation of linear polarization will allow the characterization of the orientation of molecular bonds. First results with controlled linear polarization indicate that the 11.0.2 STXM will become a powerful tool for semi-crystalline polymeric materials. Fig. 5 shows spherulitic-like domains in a thin poly-ethylene film. The relative contrast of these domains changes as the linear polarization of the EPU is switched from horizontal to vertical. Since the sample and microscope are completely unchanged, complete registration between images that contain orientation information can be achieved. A detailed analysis of images such as these and complete NEXAFS spectra will allow the determination of important parameters of the sample.

Molecular Environmental Science: metal bio-accumulation in bio-films

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Bio-films consist of colonies of microbial cells which use exo-cellular polysaccharides, proteins and nucleic acids to form an optimized environment. We are studying biofilms in order to understand how they deal with toxic elements such as metals or organic species they encounter in their environment. In addition to fundamental understanding, we hope this research will lead to practical strategies for biofilm-based remediation of polluted sites. The new undulator-based 11.0.2 STXM is an ideal tool for such studies since it can be applied to fully wet samples, it covers a wide spectral range, and because it has high sensitivity on account of excellent energy resolution and high brightness. The figure shows our first results from measurements with STXM 11.0.2. Here various metals in a river water biofilm are mapped relative to the biochemical structure of the cells and surrounding exo-cellular matrix. The Ni has been localized by bacteria from a 24 hour exposure to a flowing stream of 1 ppm nickel chloride.

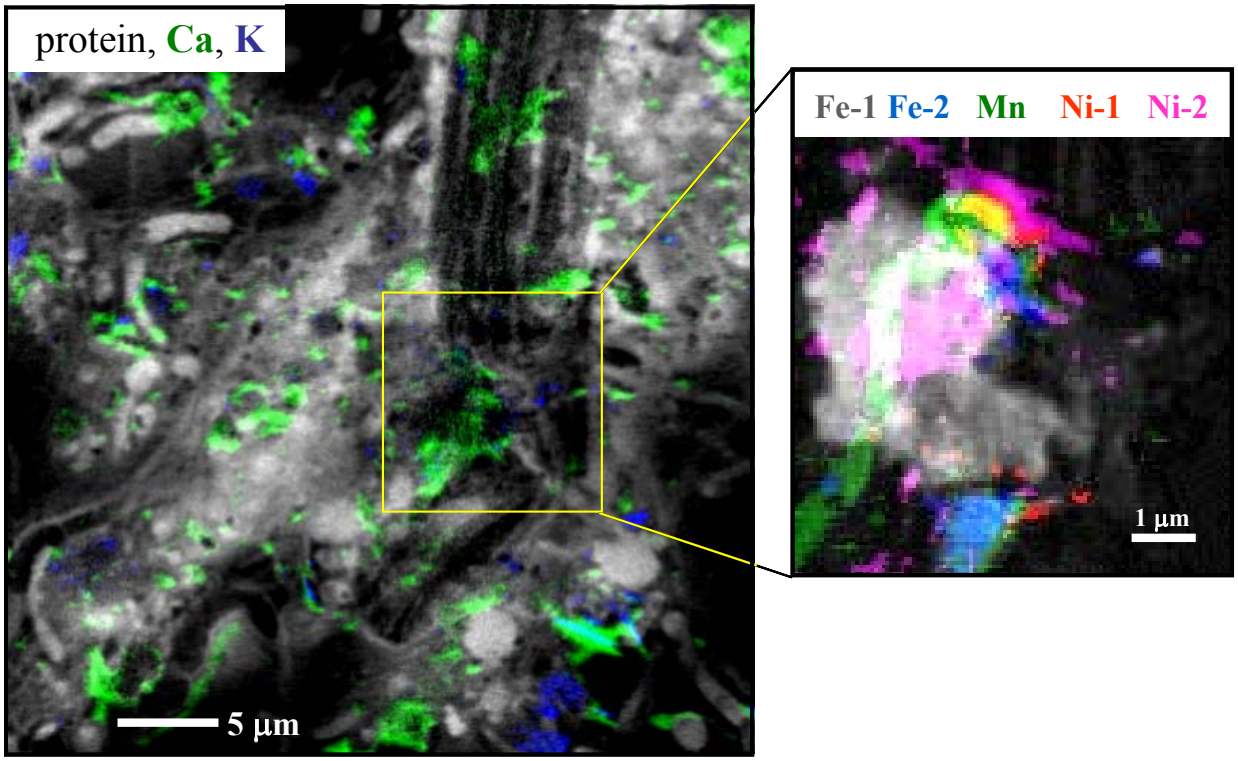

Figure 6. STXM-derived chemical maps of a river water biofilm. **(left)** Grayscale image of biological components (cells, exocellular matrix) determined from (I288-I279), the difference in images recorded at 288.2 eV (amide p* band) and 279 eV (pre-C1s), overlaid with maps of $CaCO_3$ (I352-I350) and K+ (I294-I293). **(right)** Detailed study of metal distributions in the indicated region. Image sequences recorded in the metal 2p spectral regions show multiple metal environments for Fe, and Ni. The color coded composite maps these components as well as Mn.

Materials Science: studies for the formation of silicon nanocrystals

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The wet chemistry synthesis of colloidal nanocrystals with tunable size and shapes offers exciting possibilities in material science. Nanocrystals are toolkits for the fabrication of nanodevices and nanosensors. They also allow study of properties related to quantum size effects. Well-established examples are the gram quantity synthesis of II-VI semiconductor quantum dots (CdSe,CdTe), of magnetic Co dots and disks, and of ferroelectric oxides. Silicon nanocrystals would be technologically important, but have not yet been produced on a large scale.

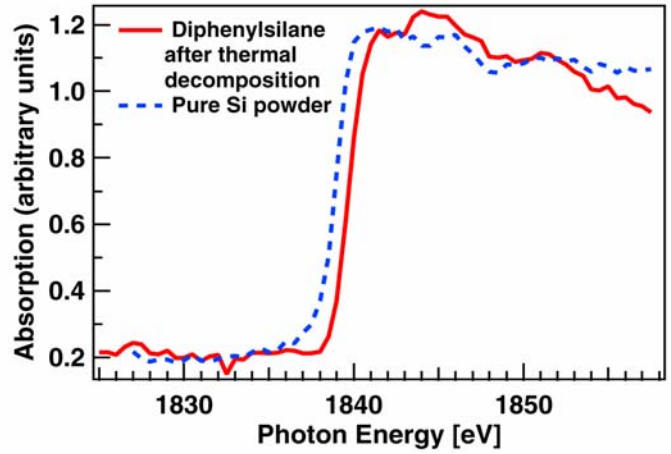

Figure 7. NEXAFS spectra extracted from image stacks on two test compounds, acquired with the11.0.2 STXM. These are silicon K-edge absorption spectra of a pure Si compound and of the result of the thermal decomposition of diphenylsilane at 400°C. Diphenylsilane is composed of two phenyl rings and two hydrogen atoms attached to a central Si atom. These chemical shifts will allow high contrast images of heterogeneous silicon chemistry.

Following an idea of Korgel *et al*. (10), we investigate the thermal decomposition of organo-silane precursors at high temperature and high pressure. As an example, we thermally decompose diphenylsilane (Phenyl2-Si-H2) in hexane at 400°C and >100 bars. Due to these extreme conditions extensive degradation of both precursor and solvent occurs. This generates new chemical species that we wish to analyze at the molecular level. Figure 7 shows the Si K-edge absorption spectra of a pure Si compound and of the result of the thermal decomposition of diphenylsilane at 400°C. The shift in the absorption edge indicates a different bonding environment for Si atoms. Tests on some molecular precursors (organo-silane compounds) at the C, O and Si K absorption edges using BL11.0.2 STXM are underway to see whether we can break the Si-C bonds and cause the condensation of Si ions into pure Si nanoparticles.

Future directions

The microscope installed at beam line 11.0.2 covers the C1s edge, where much work is done. It can also work at higher energy. The transition metal L edges. These metals are important environmental contaminants whose heterogeneous chemistry is of great interest in a wide variety of media, particularly with water present.

The availability of elliptically polarized radiation will spawn a new program in magnetic microscopy, not yet underway. The M edges of rare earth magnetic materials will be accessible. The higher flux and high photon energy will make fluorescence studies a possibility for future development.

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