10

Soft X-ray Spectromicroscopy

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Principal Contacts

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Beamline Overview

Status	Approved and funded as of December 31, 2001
Source	Elliptically polarized undulator
Monochromator	Plane grating
Spectral range	250–2000 eV
Flux at sample:	
PEEM	10^{12} photons/s/100 mA
STXM	10^{7} photons/s/100 mA
Brilliance	10^{16} photons/mm^2/mrad^2/ 0.1% bandwidth
Resolving power	3000
Spot size	
PEEM	30 µm
STXM	50 nm

Science

Spectromicroscopy is a combination of *spectroscopy*, the analysis of the way different wavelengths (colours) of light interact with matter, and *microscopy,* the imaging of matter on a scale finer than the human eye can resolve. This combination is also called analytical microscopy or near-edge X-ray absorption fine structure (NEXAFS) microscopy. The diverse research challenges facing our beamline team can best be addressed using light in the soft X-ray region (with wavelengths from 6 nm to 120 nm).

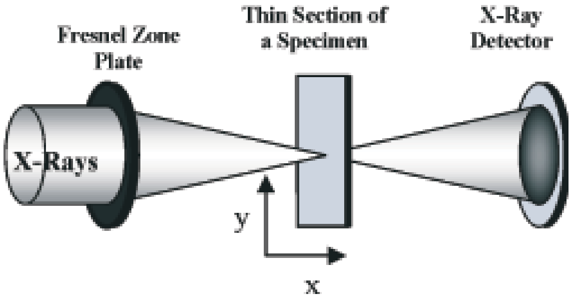

Figure 10·1 *Schematic diagram of a scanning X-ray transmission microscope (STXM). A Fresnel zone plate is used to focus the X-rays at the sample plane. To generate an image, a thin section of a specimen is raster-scanned in the focus of the X-rays. The transmitted photons are counted behind the sample by an X-ray detector.*

This beamline will be a dedicated facility for two types of soft X-ray microscopy, scanning transmission X-ray microscopy (STXM) and X-ray photoelectron emission microscopy (X-PEEM). The combination of state-of-the-art synchrotron light and two types of X-ray microscopes will allow the beamline team and other users to achieve breakthroughs in many areas, including environmental science, materials research, biology, and medicine.

The first microscope will use STXM to focus monochromatic X-rays down to 50 nm and generate images by raster scanning the sample through the fixed focal area (see Figure 10·1). The focusing element, called a zone plate, works best with the coherent (laser-like) part of the synchrotron light beam; therefore, an undulator on a third-generation synchrotron like the CLS is an optimal source. The analytical information will be generated by measuring and quantitatively analysing the changes in the images when different wavelengths are used. STXM will be used to explore many materials—including polymers, cells, plants, soil, minerals, and wood—with the goal of understanding the chemical basis for fine-scale structure, which in turn often controls the properties or function. Better understanding of the chemical basis of nano- and microstructure will be a critical part of research into creating new materials, improving medical procedures, and solving environmental problems. An illustration of the STXM technique is given in Figure 10·2.

The second technique, X-PEEM, will use the electrons produced by X-ray ionisation in the near-surface region to image the sample. As with STXM, the analytical

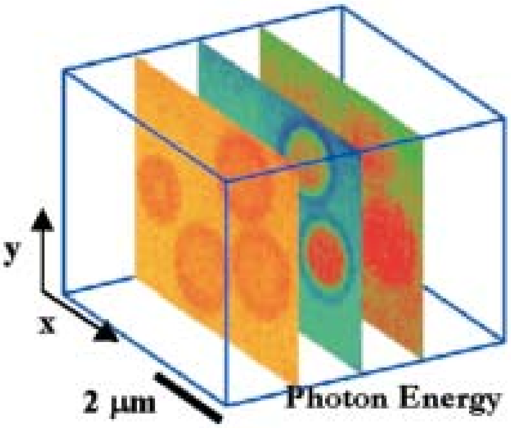

Figure 10·2 *STXM X-ray spectromicroscopy illustrated by the images at three energies of four core-shell polymer microspheres. The different chemical compositions of the core and shell regions can be determined quantitatively from the changes in the image contrast at different photon energies. Studies of structured polymer spheres are helping optimize paints, adhesives and devices for chemical separation. Data was recorded with the ALS BL 7.0.1 STXM. (Koprinarov et al.* Macromolecules ***2001,*** 34, *4424.)*

information will be obtained by varying the wavelength. Since electron lenses rather than X-ray optics will be used to generate the magnified image, the requirements for the synchrotron light will be less demanding. The X-PEEM will be mobile, and thus can potentially be mounted on any of the CLS beamlines., but its home will be the soft X-ray spectromicroscopy beamline.

X-PEEM detects photo-ejected electrons, which can only escape from a very thin surface layer (from 1 to 5 nm, depending on the material). It will be used to study surface and thin film phenomena, such as the protective films formed by oil additives in car engines; magnetic structures, such as those used in the computer industry; and polymers in contact with blood, including the various materials used in artificial hearts. X-PEEM and STXM are related and complementary techniques.

The mission of the spectromicroscopy group is twofold: to build a high-performance soft X-ray spectromicroscopy beamline and the associated microscopes, and to develop a strong national and international user community through collaborative research, with participation by academic, industrial and government scientists. Several members (including Hitchcock and Tyliszczak) have recently participated in the design, construction and commissioning of a state-of-the-art STXM at the ALS, as reported later in this chapter. Many of the advances developed at that facility will be used in the STXM beamline at the CLS.

The X-PEEM microscope will be a commercially produced instrument, and has been purchased through an NSERC major installation grant awarded to Stephen Urquhart (U. of Saskatchewan). It will be used at the SRC (U. of Wisconsin-Madison) until it can be installed on the X-PEEM branch line at the CLS in 2004.

Layout and Instrumentation

Figure 10·3 gives a simplified schematic layout of the spectromicroscopy facility. A 1.6 m long, Apple-II-type elliptically polarized undulator (EPU) will provide photons with a user-specified polarization (from circular polarized to plane polarized, with user choice of the polarization plane). The EPU will be used in chicane mode and will be placed upstream of the centre of the 10ID straight section. The EPU will use a new magnetic termination scheme that minimizes the impact of EPU magnetic field changes on the electron beam trajectory; this will allow the EPU to be operated in “synchronized mode”, with gap and phase control by the user. The predicted EPU performance is shown in Figure 10·4.

The first mirror will be a water-cooled cylinder that will deflect the beam inboard by 3 degrees and will produce light almost parallel in the vertical direction. This parallel beam will be directed to a plane grating monochromator (PGM) with no entrance slit, to be built according to an advanced design currently under construction at the ALS. This scheme will give a substantial reduction in the thermal power load on the PGM optical components, as well as flexibility for experiment-driven choices between intensity conservation, higher-order suppression, and energy resolution. The nominal energy resolution will be 3000, but this may be enhanced to 7000 if needed. Based on optical modeling calculations, the expected intensity will be 10^{12} photons/s in a 20 µm spot on the sample for X-PEEM and 10^{8} photons/s in a 50 nm spot on the sample for STXM; this will occur over essentially the entire intended photon energy range of 250 to 2000 eV. Further details are given in Figure 10·5 and in the following section on the performance of this beamline.

The output of the PGM will be directed toward either of two branches, using one of two toroidal focusing mirrors. The longer STXM branch will occupy the outboard side of 10ID.1 beamline, and the shorter X-PEEM branch will occupy the inboard side. Insertion of the X-PEEM focusing mirror into the beam will deflect the beam from the STXM to the X-PEEM branch. This arrangement will give reasonable separation between optical components, preserve the STXM performance, and provide good access to the X-PEEM endstation. In addition, another experimental chamber can be substituted for the X-PEEM endstation as needed. The two endstations together will form a dedicated facility for soft X-ray microscopy.

The scanning transmission X-ray microscope will be based on the very successful BL 5.3.2 STXM recently brought into operation at the ALS. The X-PEEM will be a commercial instrument made by Elmitec GmbH, and will be operated at the SRC from mid-2002 until the X-PEEM branch is commissioned. More details on the STXM at the ALS and the X-PEEM at the SRC are provided later in this chapter.

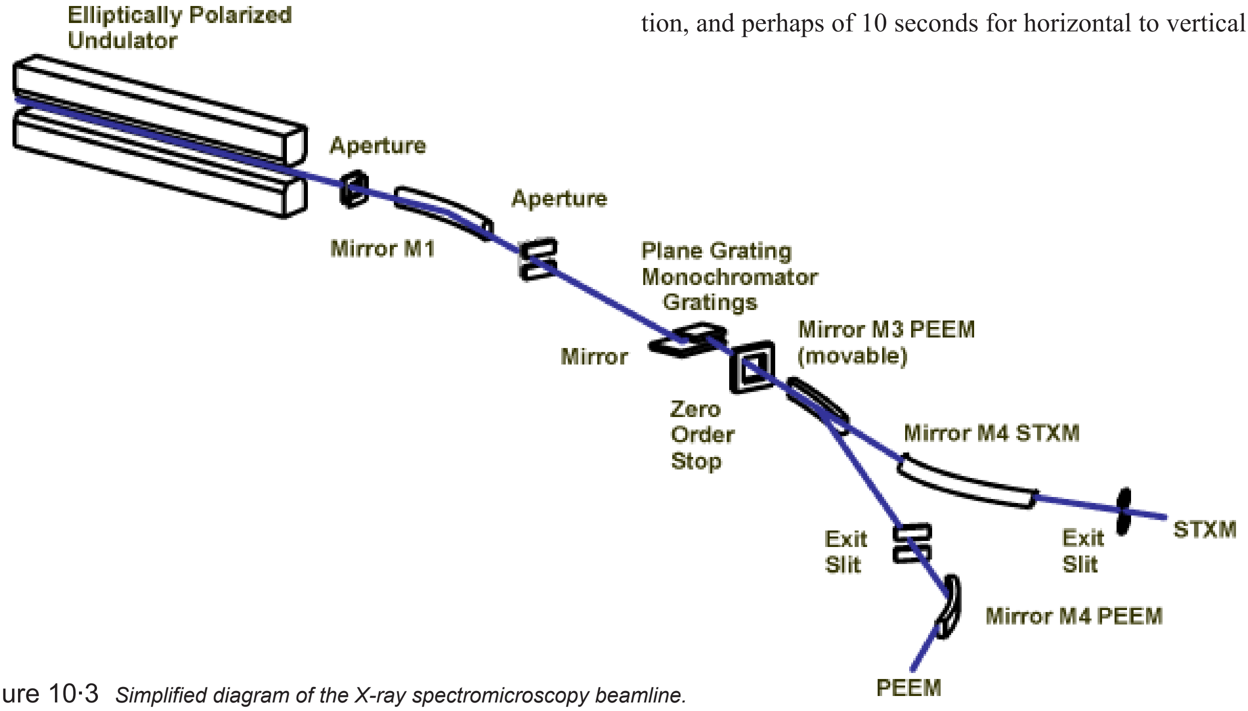

Figure 10·3 *Simplified diagram of the X-ray spectromicroscopy beamline.*

Performance

Energy range of the EPU and PGM

This PGM is designed to operate from at least 250 to 1900 eV. It is also expected to have the capability to operate down to 100 eV (to access the silicon 2p edge) and up to 2500 eV (to access the phosphorus 1s and sulfur 1s edges), although with reduced performance outside the design range.

Polarization control

The linear polarization will be horizontal over the whole range (100% polarization is expected). The circular polarization control will have user-selectable helicity (L/R) from 600 to 900 eV; the polarization will be 100% circular on axis in the fundamental. The orientation of the linear polarization will be fully adjustable over as wide an energy range as possible, and the minimum range will be 250 to 600 eV. Arbitrary polarization changes will be under user control (subject to imposed safety limits).

The time to execute polarization changes will be as small as possible. Based on a similar device at the ALS (which does not have advanced ESRF-type termination for isolating the effect of EPU changes from the lattice), it should be possible to achieve switching times of a few seconds for a change from left to right circular polarization, and perhaps of 10 seconds for horizontal to vertical.

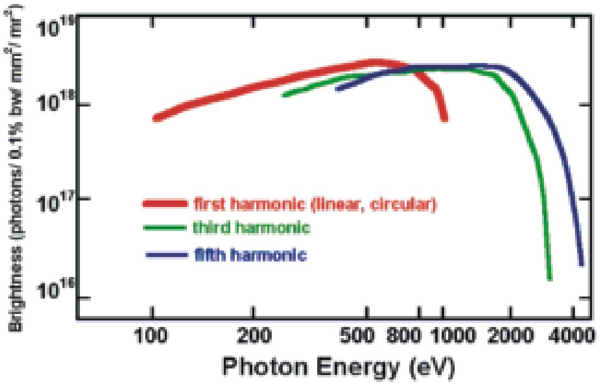

Figure 10·4 *EPU brightness as a function of energy for the first, third and fifth harmonics. Full circular polarization will be available only over the range of the first harmonic.*

Resolving power and intensity

The resolving power for this beamline will be 3000 (typical energy resolution). At this resolving power, the band pass will be 100 meV at 300 eV, 200 meV at 600 eV, and 0.61 eV at 1840 eV.

Maximum flux will be required for such resolving power. For STXM, the criterion for beam flux on the sample will be 10^8 photons/s into a 50 nm zone-plate-focused spot at $E/\Delta E = 3000$. With a 200 µm circular zone plate, an overfilling factor of 3, and efficiencies of windows and zone plate to give ~1% overall transmission, this specification requires 10^{10} photons/s/mm^2 at the input of the zone plate. For X-PEEM at $E/\Delta E = 3000$ (100 meV bandwidth in the carbon 1s region), the flux will be 10^{12} photons/sec into an approximately circular 30 µm spot on the sample.

STXM optimization will have priority if there are optical design conflicts among the branches, since it will be more sensitive to alignment and brightness issues.

Beam size

For STXM, the beam size at the zone plate must be large enough to provide even illumination over an overfilled 200 µm zone plate. The overfill factor should be minimized to reduce intensity loss.

For X-PEEM, a beam spot of about 30 µm in diameter on the sample will be required, along with the ability to defocus the beam spot on the sample to allow for viewing of larger areas and to minimize radiation damage.

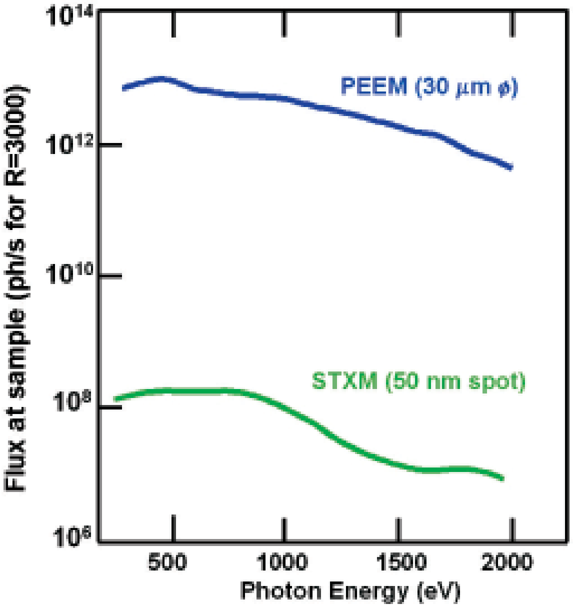

Figure 10·5 *Predicted flux at the sample at a nominal resolving power of 3000, for the projected conditions of the CLS storage ring in 2008. Lower line: the STXM intensity in the 50 nm focus spot. Upper line: the X-PEEM intensity in the minimum field of view of the microscope (30 µm). Loss factors (real phase space acceptance; optical reflectivity, efficiency, and transmission) have been taken into account. The EPU radiation in first order (200–1000 eV), third order (600–1800 eV), and fifth order (>1500 eV) was used.*

Stephen Urquhart (University of Saskatchewan) explains X-ray microscopy to Rob Slinger (CLSI) and to Paul Martin, Canada's Minister of Finance.

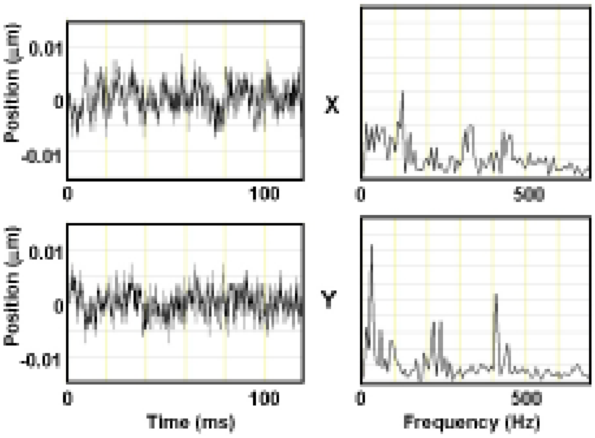

Figure 10·6 *Tests of stability of the sample position using interferometric control (T. Tyliszczak, February, 2001).*

Endstations

There will be two branch lines and at least two endstations. The STXM will be permanently installed on the first branch line. The X-PEEM will normally be located at the second branch line, but it will also be used on other beamlines (such as the VLS-PGM and the SGM). Various compatible endstations may be used on the X-PEEM branch line.

Beamline Team Research Activities

ALS 5.3.2 STXM: the basis for a state-of-the-art instrument at the CLS

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This section reports on the work of Harald Ade (NCSU), David Kilcoyne (NCSU), Tony Warwick (ALS), Keith Franck (ALS), Mike Kritscher (ALS), Erik Anderson (LBNL), Adam Hitchcock (McMaster U.), Tolek Tyliszczak (McMaster U.), and Peter Hitchcock (McMaster U.).

Over the past three years, a qualitatively new design of scanning transmission X-ray microscope has been conceived, built and commissioned at the Advanced Light Source. A dramatic improvement in performance has been achieved by introducing laser interferometry to control the relative spacing of microscope elements. This allowed a mechanical precision of approximately 10 nm, well within the current diffraction-limited zone plate resolution of about 40 nm. However, the resolution of future zone plates is expected to be as small as 10 nm.

The interferometer is a great advance over previous systems (the old BL 7.0 STXM at ALS and X1a at NSLS).

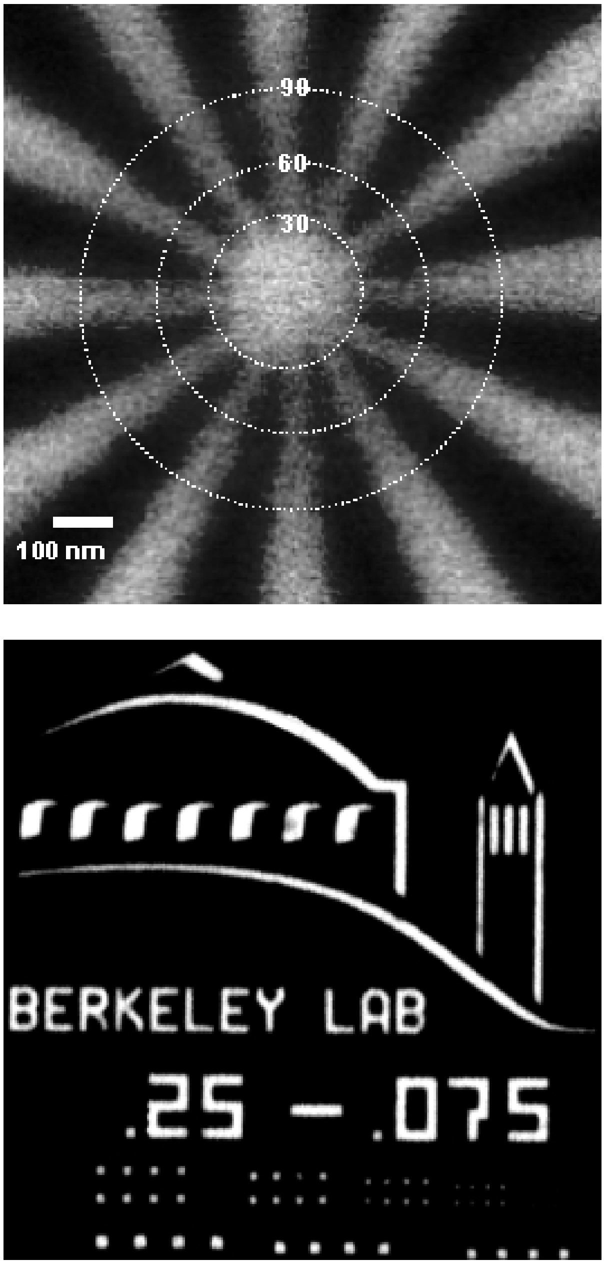

Figure 10·7 *Resolution demonstration using two test patterns (electron-beam-generated patterns in gold deposited on silicon nitride). The star test pattern shows the diffraction-limited resolution predicted for the zone plate (35 nm outer zones, 150 μm wide). Zone plate and test patterns were prepared by Erik Anderson et al. (CXRO, LBNL).*

With earlier instruments, one could image at a fixed photon energy and get spatial resolution close to the diffraction-limited zone plate performance. However, the spatial resolution is degraded for chemical analysis applications, because the focal length of a diffractive zone-plate focusing element is a function of X-ray wavelength. Therefore, with those instruments it is not possible to change photon energy while maintaining the focused X-ray spot on the same place on a sample, or to image at successive energies over the same *x-y* frame. Over a typical carbon 1s NEXAFS scan from 280 to 310 eV, the focal length changes by up to 300 µm, thus requiring an identical displacement of the zone plate along the X-ray beam axis while still preserving the lateral position of the zone plate (relative to the sample) to within the spatial resolution of 50 nm. Achieving linearity of 1 in 10^4 for all the axes simultaneously would demand exceptional mechanical systems. Indeed, the experience at both the ALS and the NSLS microscopes has been that spatial resolution in point spectral mode is rarely better than 200 nm, and that one needs to use software to correct for image-to-image misalignment, with concomitant residual resolution degradation.

The solution that was developed at the ALS BL 5.3.2 STXM was to introduce a 2-D laser interferometer system that continuously monitors the relative (*x,y*) position of the zone plate and the sample. In the BL 5.3.2 STXM, the interferometer is used as part of the feedback control loop for the fast piezo stage, which is used to position and scan the sample when making images. This system provides stability of better than 10 nm with response times up to 100 Hz (see Figure 10·6). Thus, it not only eliminates energy-to-energy image position errors, but also helps to desensitize the microscope to vibrational or other environmental noise.

With this mechanical-optical control system [1–3], accompanied by advanced control and data acquisition software [4], the BL 5.3.2 STXM is able to achieve diffraction-limited spatial resolution. The images of a gold test pattern (Figure 10·7) indicate a spatial resolution for high-contrast objects of better than 40 nm, which is the theoretical diffraction-limited resolution of the zone plate used. More significantly (for analytical applications), the interferometry allows the 5.3.2 microscope to retain image registry at all photon energies. As an example of the level of positional stability achieved with the interferometry system, Figure 10·8 compares linescan spectral data acquired at ALS beamline 5.3.2 with similar data acquired with the old ALS BL 7.0.1 STXM [5]. The spatial and photon energy ranges were similar; the common sample (courtesy Ed Rightor, Dow Chemical) was polyurethane containing nanoscale filler particles. In each case, the raw data—the position along the inset line versus photon energies—are plotted. Clearly, the ability to determine the NEXAFS spectra at high spatial resolution is greatly enhanced by the improved performance of the BL 5.3.2 STXM [6,7] relative to earlier STXM instruments.

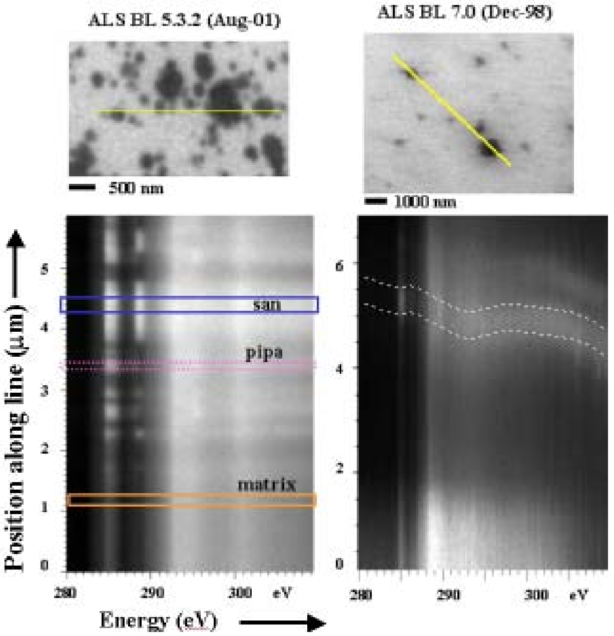

Figure 10·8 *Comparison of "pointing precision" of the old ALS BL 7.0.1 STXM and the new ALS BL 5.3.2 STXM using polymer samples ("san" = styrene-acrylonitrile; "pipa" = poly-isocyanate poly-addition product; matrix = low water poly-urethane). The two lower "images" plot the linescans measured with each instrument. The successive horizontal lines in the lower figures are the spectra at pixels nominally along the lines marked in each of the upper figures, which are the true optical density images of the samples (BL 5.3.2 = pipa and san; BL 7.0.1 = pipa only; both in the same matrix). The waviness of the signal in the horizontal direction in the linescan of the old BL 7.0.1 STXM is caused by mechanical limitations that result in drifting of the X-ray spot on the sample. In contrast, the linescan of the new BL 5.3.2 STXM has negligible waviness in the horizontal direction. This is because the interferometric control in the BL 5.3.2 STXM provides precise positioning at all photon energies. It also provides significant dynamic compensation for vibrations that degraded the performance of the old BL 7.0.1 STXM.*

Table 10·1 Co-applicants on the NSERC Major Installation grant application for X-PEEM

Co-applicants	Research Interests
University of Saskatchewan	
Stephen Urquhart (PI)	XNCD, organic microanalysis
Katie Mitchell	Surface physics
Alex Moewes	Magnetism
Bernie Kraatz	Bio-electronic surfaces
Roberta Silerova	Ultrathin film thermodynamics
University of Western Ontario	
Mike Bancroft	Tribology
Peter Norton	Tribology
T. K. Sham	Organic electronic devices
McMaster University	
Adam Hitchcock	Blood contact polymers; polymer surfaces
Université Laval	
Denis Roy	Ion modified HOPG surfaces
INRS (Université du Québec)	
Daniel Guay	Nanocomposite electrocatalysis
University of Alberta	
Ron Cavell	Inorganic & magnetic materials

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[1] T. Tyliszczak; H. Ade; S. Fakra; K. Franck; A. P. Hitchcock; P. Hitchcock; A. L. D. Kilcoyne; W. F. Steele; T. Warwick. Laser Interferometric Control of Scanning X-ray Microscopes. *Synchrotron Radiation Instrumentation International,* Berlin, August, 2000.

[2] T. Warwick; H. Ade; S. Fakra; A. P. Hitchcock; P. Hitchcock; K. Kaznacheyev; A. L. D. Kilcoyne; W. F. Steele; T. Tyliszczak. New Scanning Transmission X-ray Microscopes at ALS. *SPIE,* San Diego, July, 2001.

[3] A. L. D. Kilcoyne; H. Ade; A. P. Hitchcock; P. Hitchcock; T. Tyliszczak; S. Fakra; K. Franck; W. F. Steel; T. Warwick. Interferometric Scanning Transmission X-ray Microscopy at the ALS. *Synchrotron Radiation Instrumentation,* August, 2001, Madison, WI.

[4] T. Tyliszczak; P. Hitchcock; A. L. D. Kilcoyne; H. Ade; A. P. Hitchcock; S. Fakra; W. F. Steele; T. Warwick. Control and Acquisition Systems for New Scanning Transmission X-ray Microscopes at the ALS. *Synchrotron Radiation Instrumentation,* August, 2001, Madison, WI.

[5] A. P. Hitchcock; I. Koprinarov; T. Tyliszczak; E. G. Rightor; G. E. Mitchell; M. T. Dineen; F. Hayes; W. Lidy; R. D. Priester; S. G. Urquhart; A. P. Smith; H. Ade. Copolymer polyol particles in polyurethanes studied by soft X-ray spectromicroscopy. *Ultramicroscopy* **2001,** *88,* 33.

[6] T. Warwick; H. Ade; A. L. D. Kilcoyne; M. Kritscher; T. Tyliszczak; S. Fakra; A. P. Hitchcock; P. Hitchcock; H. A. Padmore. A Bend Magnet Beam Line for Diffraction-Limited STXM Illumination at the Advanced Light Source. *J. Synchrotron Radiation* **2002,** submitted.

[7] A. L. D. Kilcoyne; T. Tyliszczak; R. Steele; A. Peter Hitchcock; S. Fakra; K. Frank; C. Zimba; E. Rightor; G. Mitchell; I. Koprinarov; E. Anderson; B. Harteneck; Adam P. Hitchcock; T. Warwick; H. Ade. Interferometrically Controlled Scanning Transmission Microscopes at the Advanced Light Source. *J. Synchrotron Radiation* **2002,** in preparation.

Table 10·2
Soft X-ray spectromicroscopy beamline team

Team members	Applications and techniques
Canadian Light Source	
Emil Hallin (CLS Beamlines Manager)	
Kostantin Kaznacheyev (Beamline Scientist)	Magnetic materials (STXM, X-PEEM)
McMaster University	
A. P. Hitchcock (BIMR; Beamline Team Leader)	Polymers (STXM, X-PEEM)
H. Stöver (Chemistry)	Designer polymers (STXM)
T Tyliszczak (BIMR)	Biomaterials (STXM, X-PEEM)
NRCan	
J. Brown (CANMET)	Resource technologies (STXM, X-PEEM)
State University of New York-Buffalo	
J. Gardella (Chemistry)	Biomaterial interfaces (STXM, X-PEEM)
University of Saskatchewan	
S. G. Urquhart (Chemistry)	Polymer microstructure (STXM, X-PEEM)
University of Alberta	
R. G. Cavell (Chemistry)	Alberta applications (STXM, X-PEEM)
University of Guelph	
J. Dutcher (Physics)	Self-organisation (STXM)
University of Nebraska-Lincoln	
B. Robertson (Mechanical Engineering)	Magnetic thin films (X-PEEM)
P. A. Dowben (Physics)	Magnetic thin films (X-PEEM)
S. Adenwalla (Mechanical Engineering)	Magnetic thin films (X-PEEM)
INRS (Université du Québec)	
D. Guay (Énergie et Matériaux)	Nanomaterials for Electrocatalysis (X-PEEM)
Université Laval	
D. Roy (Physique)	Ion modified materials (X-PEEM)
University of Western Ontario	
G. M. Bancroft (Chemistry)	Tribology (X-PEEM)
M. Kasrai (Chemistry)	Tribology (X-PEEM)
P. R. Norton (Chemistry)	Tribology, nanoproperties (X-PEEM)
R. Martin (Chemistry)	Plant materials (STXM)

X-PEEM: the instrument and the implementation schedule

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In the fall of 2000, a multi-university team lead by Stephen Urquhart (Dept. of Chemistry, University of Saskatchewan) submitted an NSERC Major Installation

Table 10·3 Spectromicroscopy design team

Role	Name	Institution	Experience
ID Designer	Ingvar Blomqvist	CLS	Danfysik
CLS Beamlines Manager	Emil Hallin	CLS	SAL; CSRF; PNC-CAT; CLS Work Package #6 leader
Beamline Team Leader	Adam Hitchcock	McMaster U.	STXM and X-PEEM user (ALS, SRC, NSLS)
Beamline Development Scientist	Konstantin Kaznacheyev	CLS	ELETTRA; Photon Factory; NSLS
Controls; Interfacing; STXM Design	Tolek Tyliszczak	McMaster U.	ALS 5.3.2 beamline; STXM
X-PEEM Coordinator	Stephen Urquhart	U. of Saskatchewan	STXM and X-PEEM user (NSLS, ALS, SRC)
Beamline Design Consultant	Tony Warwick	ALS	Deputy Director, ESG (ALS); Designer and Manager of ALS BL 7.0, 7.3, and 11.0

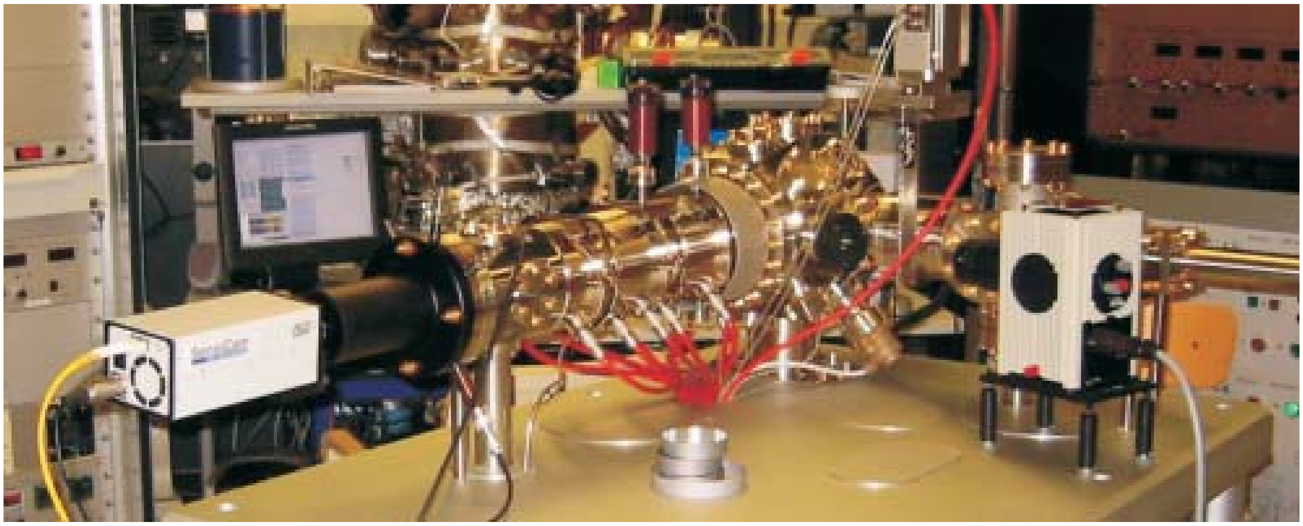

Figure 10·9 *A view of the Elmitec PEEM.*

grant application for a photoelectron emission microscope and associated sample preparation capabilities (see Table 10·1). An on-site review was conducted in January of 2001, and NSERC subsequently awarded $680,000 for this facility.

The commercially available instrument with the highest performance, an Elmitec PEEM (Figure 10·9), was selected and is scheduled to be delivered to the Synchrotron Radiation Centre (University of Wisconsin-Madison) by May of 2002. It will be used at the CSRF and other SRC beamlines for about two years.

This endstation will be installed on the X-PEEM branch line of the CLS spectromicroscopy facility, after the performance specifications of the beamline are achieved and stable operating conditions exist.

Beamline Team and Design Team

Table 10·2 lists the beamline team, which has defined the core-group scientific program and the instrumental parameters. Table 10·3 lists the beamline design team.