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Introduction

Third generation synchrotron sources of soft x-rays provide an excellent opportunity to apply established x-ray spectroscopic materials analysis techniques to surface imaging on a sub-micron scale. This paper describes an effort underway at the Advanced Light Source (ALS) to pursue this development using Fresnel zone plate lenses. These are used to produce a sub-micron spot of x-rays for use in scanning microscopy. Several groups have developed microscopes using this technique [1]. A specimen is rastered in the focused x-ray spot and a detector signal is acquired as a function of position to generate an image. Spectroscopic capability is added by holding the small spot on a feature of interest and scanning through the spectrum.

We are pursuing two spectroscopic techniques, which together provide a powerful capability for light element analysis in materials science.

1) Near Edge X-ray Absorption Spectroscopy (NEXAFS) [2] is a relatively new technique for materials science. It gives very characteristic information about light element chemistry, and the interaction of these atoms with their neighbors. Core electrons are excited into states near threshold by x-ray absorption. As the photon energy is varied, the structure of the threshold density of states is seen in the absorption spectra. Organic molecules typically exhibit identifiable peaks corresponding to molecular orbitals localized at specific atomic sites. Their K-edge spectra can be calculated [3], and exhibit strong dependence on the polarization of the photon and the orientation of the molecules. Ionically bonded species

have L-edge absorption spectra which show strong charge-state dependence. Crystal field effects are seen in ordered solids [4].

2) X-ray Photo-electron Spectroscopy (XPS) [5] is a well established technique giving quantitative measurements of the concentration of species and quantitative measurements of core level chemical shifts. It is in wide use for materials analysis. Modern laboratory sources can be focused and monochromatized, so that surface imaging XPS spectroscopy can be performed in the laboratory with a spatial resolution of about 10 microns. In this work we extend the technique to explore sub-micron spatial scales. XPS is a surface sensitive technique which can give information as a function of depth when combined with sectioning or sputter profiling.

These two spectroscopies are applied in a pair of scanning zone-plate microscopes which operate in tandem at undulator beamline 7.0 at the ALS. Figure 1. shows this facility. The undulator source serves a high resolution spherical grating monochromator [6] with high dispersion, designed for spectroscopy. This means that microscopic measurements which do not need the high (1:5000) spectral resolution pay a flux penalty (of about a factor of ten). Nevertheless the count rates in these microscopes are about ten times higher than previously available. The high brightness illumination provides these higher count rates by delivering a larger fraction of the photon flux into the phase space acceptance of the microscopes. As a result, the optics are overfilled less. While the flux is higher, spectral and image quality is more sensitive to beam motion.

The zone plates [7] currently in use are from a batch made at IBM, Yorktown Heights, in 1995 (Courtesy E. Anderson). These lenses are 0.2mm in diameter (D), 80nm outer zone width (δr_N) with a 0.06mm diameter central stop. The zones are 100nm thick, made from gold on a 100nm silicon nitride membrane. They are intended as amplitude zone plates with opaque zones. They are used with photons from 150eV to 900eV. At the shorter wavelengths (λ) the zones are not opaque and the diffraction efficiency is reduced. The first order focal length is given by

$$f = D \delta r_N / \lambda$$

and has a value of 4mm at the carbon edge.

The scan stages in use are monolithic x/y flexures (from Queensgate Instruments, Bracknell, RG12 1RB, UK), driven by piezo-electric transducers with capacitance micrometers built into the stage. The moving platen nominally traverses 100microns in x and y, although we find the range reduced somewhat to about 80microns as the piezo-

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electric actuators age. The stage is driven stepwise, and the small-step settle time of the capacitance encoder feedback loop is about 2ms. The stage is intended to be used about the center of its moving platen, but we have moved it 5cm off axis in each microscope. This introduces Abbe errors whereby the slight rotation of the platen converts to unwanted transverse motion at the end of the lever arm, and gives images sheared by about 7%.

The Scanning Transmission X-ray Microscope (STXM)

Figure 2. illustrates the zone plate scheme employed in STXM. The lens is outside a Si_3N_4 vacuum window (courtesy D. Ciarlo, Lawrence Livermore National Laboratory) 160nm thick. We are presently using lenses with 80nm outer zone width, and a corresponding diffraction limit to the spatial resolution of about 100nm. The lens is illuminated through a pinhole 3m upstream, which can serve as the object to be demagnified onto the sample. Alternatively, the pinhole can be removed to increase the flux with barely noticeable degradation of the spatial resolution, since the pinhole is illuminated by approximately parallel light.

The order sorting aperture (OSA) is precisely positioned on the optical axis (+/-2 microns) to allow only the first order diffracted focus to reach the sample. This aperture is a photo-sensitive element which generates a signal (a few pA) proportional to the illumination intensity for spectral normalization against the effects of beam motion in the beamline. We have measured 2×10^7 photons/second with a spectral width 1/3000 in the zone plate first order focus spot at 300eV, with the storage ring running at 1.5 GeV, 400mA. At higher photon energies the intensity increases, as the windows become more transparent, until the beamline output decreases above 500eV [6]. Images are typically acquired with a counting time of 10ms per pixel. NEXAFS spectra are acquired with a counting time of several hundred ms per energy point. Coordinated undulator and monochromator moves take about 250ms to complete, during which time a fast mechanical shutter closes to protect radiation sensitive samples from unnecessary exposure.

The transmission geometry is the most efficient use of photons for an absorption spectrum, well suited to the study of radiation sensitive samples. We find most organic samples are susceptible to radiation damage, with changes seen in the absorption spectra after several measurements. Control of the dose is essential and filters are employed in the beamline to optimize the count rates.

Measurements in transmission are bulk sensitive, so that surface contamination is not a concern, this allows the operation of the microscope at atmospheric pressure, in air or helium, with hydrated samples as appropriate. This last point is of crucial importance for problems in environmental science, when the presence of water is often central to the chemistry of contamination.

Sample preparation becomes complicated for transmission measurements. The sample thickness must contain about one absorption length of the species of interest at the edge to be measured, otherwise the signal-to-noise ratio is unfavorable. The spectra are measured with the sample in and out, each spectrum has its dark counts subtracted, is optionally normalized to the OSA signal and the logarithmic ratio gives the absorption spectrum. Organic solids have been sliced by micro-tome as part of an ongoing polymer studies program. Harder materials may require ion milling. Wet cells have been built to contain the appropriate thickness of aqueous sample, sandwiched between Si_3N_4 windows.

Tuning the beamline for operation of this microscope is tricky because the line is shared with other spectroscopy groups. Figure 3. shows the measured illumination pattern on the zone plate lens, with the first order light coming to a focus in the center of this image. The image is made by scanning the OSA prior to its careful positioning on the optical axis.

The most difficult mechanism involved in this microscope is the flexure which translates the zone plate longitudinally through 0.5mm to remain in focus as the photon energy is changed during a NEXAFS scan. This mechanism inevitably has some unwanted sideways run-out (about 0.4 microns) which is reproducible and compensated by programmed sideways motion of the sample during the spectral scan. The resulting lock-in (0.2 microns) allows spectra to be measured with some confidence on features uniform over regions as small as 0.5 microns. We are presently making a transition to finer zone plates (spatial resolution improved by a factor of 2) with shorter focal lengths (by a factor of 4) so that the spatial resolution will be improved and this difficult translation will be smaller.

Photons are detected in transmission by one of three detectors.

- 1) An analog silicon photo diode (from International Radiation Detectors, Torrance, CA90505, USA) for full intensity measurements. This detector is essentially 100% efficient above 100eV except for a thin oxide layer.
- 2) A gas proportional counter (Ar/CO₂) with a Si_3N_4 window. This is about 5% efficient at 300eV, where the pulse heights are well above the noise. This detector is used at reduced intensity (eg 300kHz counting rate).

3) An optically coupled high rate avalanche photo diode which uses a microscope to collect visible light from a phosphor behind the sample. This scheme is under development. The detector is in use and the choice of luminescent phosphor is being explored.

Figure 4. shows a case study illustrating the STXM capabilities. Kevlar fibers have been studied before [8]. In this case the polarization/orientation sensitivity is explored at the K edge of three atoms in the molecule; carbon, oxygen and nitrogen. The latter two measurements require a pure helium environment to remove atmospheric absorption effects.

The Scanning Photo-Emission Microscope (SPEM)

Figure 5. illustrates the zone plate scheme employed in SPEM. Here the sample is stationary during imaging and the zone plate is rastered in the illumination field to carry the focused spot across the sample surface. The illumination is of the order of 1mm diameter and the raster range is 100x100 microns. The electron spectrometer can view the entire range of the image area and collects photo-electrons at 60 degrees from the sample normal. The OSA is within 0.5mm of the sample surface, and the zone plate assembly is cut back on one side to allow a line of sight for the spectrometer. NEXAFS capability is included by means of a flexure to carry the zone plate 0.5mm longitudinally to retain the focus condition as the photon energy changes. The OSA moves away from its optimum longitudinal position during a NEXAFS scan but not so far as to intercept the first order light.

The OSA is fixed to the zone plate, with the focal length built in to the assembly. Different photon energies require different zone-plate/OSA combinations with different built-in focal lengths (e.g. 620eV for survey spectra including oxygen 1s photoelectrons, 270eV to 310eV for carbon K edge NEXAFS measurements). Five zone plates will be mounted together on a monolithic array with precisely parallel optical axes (to +/-1mrad), interchangeable under computer control. So far we have operated the microscope with two zone-plate/OSAs aligned in this way. With a stationary sample we can provide heating and cooling for measurements above and below room temperature. Liquid nitrogen is introduced to achieve 130 degrees Kelvin, heating will be limited by the proximity of the zone plate array, to about 200 degrees Celsius. So far, measurements have been made only at room temperature. SPEM allows us to perform quantitative XPS measurements of atomic concentration and core level chemical shifts over regions of the sample surface as

small as the spatial resolution of the zone plate lens (currently 0.3 microns has been observed).

NEXAFS spectra are made with the same difficult longitudinal motion of the lens as for STXM. These will be surface NEXAFS measurements made in electron yield mode. We have not made use of this feature yet, but look forward to complementary XPS/NEXAFS studies of the same sample.

Once the instrument chamber is positioned correctly the steering of the photon beam into SPEM is straight forward. The zone plate lens is surrounded by phosphor and viewed by a magnifying video telescope which shows the x-ray illumination pattern. The zone plate array can be lowered out of the beam and the sample surface can be observed with the same video system, allowing visible fiducial marks on the sample to be used to position the region of interest within the 100x100 micron range of the scan stage. Figure 6. shows this navigation scheme in action.

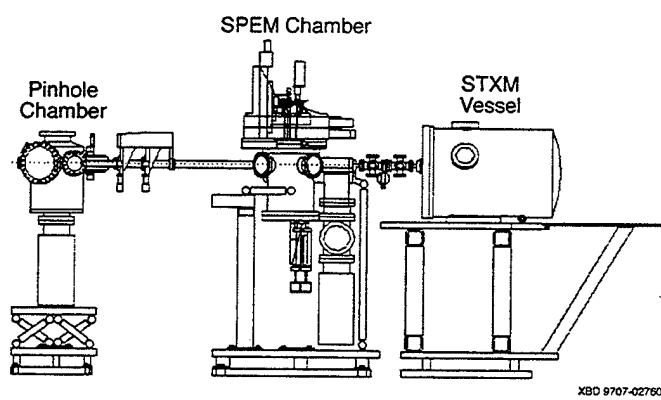
XPS spectra are measured with typical photo-peak count-rates of 70,000 counts/second (Au 4f at 420eV photon energy).

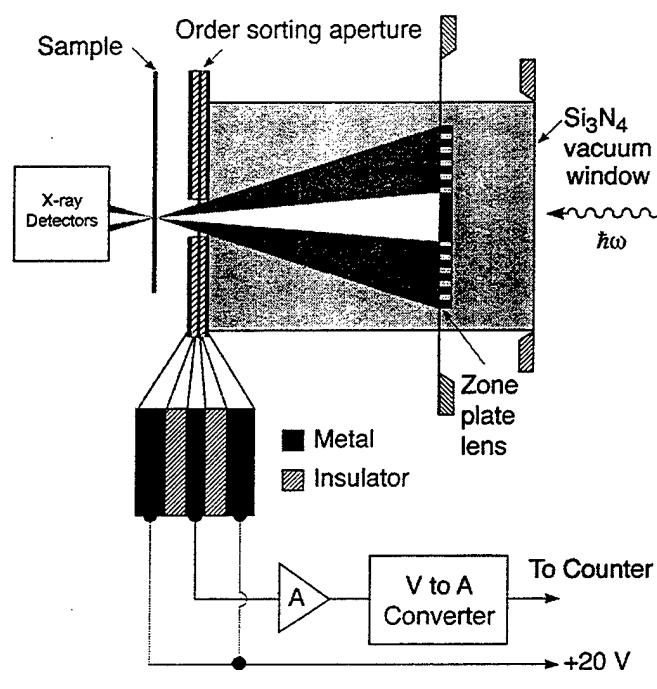
Sample charging is partially neutralized by the proximity of the zone plate assembly to the sample surface (which serves as a source of low energy electrons) and by an electron flood gun. Remaining charging shifts are corrected relative to the photo-emission peaks of contaminant carbon or to a Fermi edge. Sample sputtering and annealing is provided in a preparation chamber adjacent to the microscope chamber. The instrument operates at 5×10^{-10} Torr

Figure 7. shows a SPEM case study in which an Al/Ti melt has been allowed to solidify on a graphite substrate [9]. The image of the polished section shows the aluminum metal, precipitates of Al₃Ti alloy and the graphite interface, with carbide formation. Different core level chemical shifts are observed from the Al, the Al₃Ti alloy and the carbide region. Topography is visible in the image because of the sideways collection of electrons. The harder alloy precipitates are proud of the metal surface after polishing. In this case sputtering has removed the adventitious carbon contamination but the surface is still oxidized.

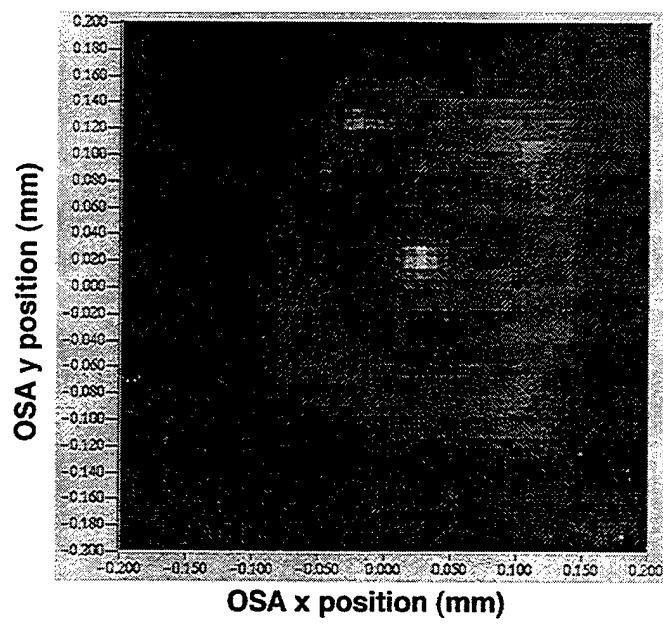
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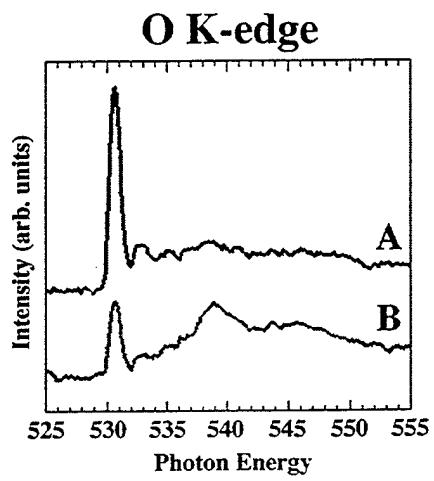
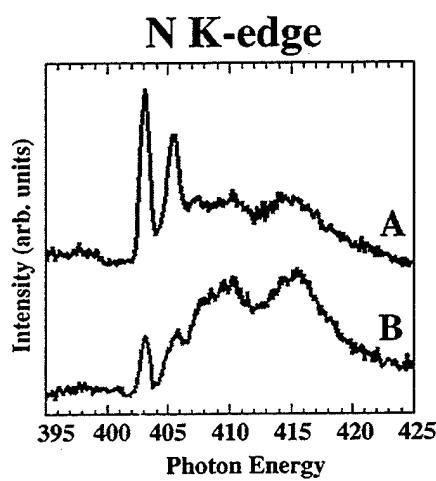
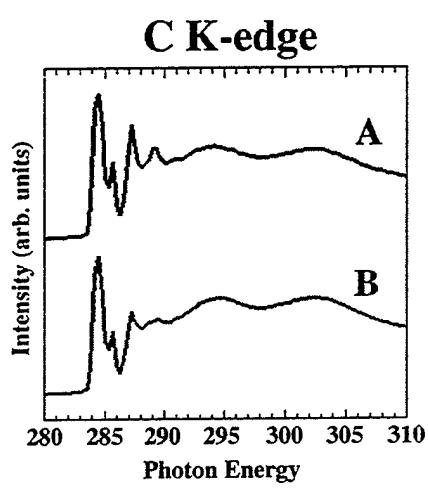
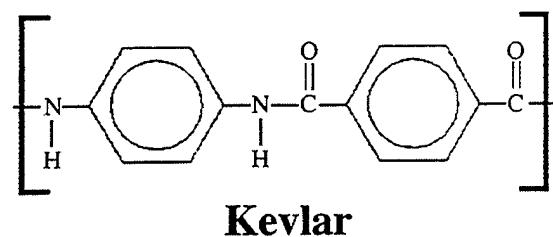
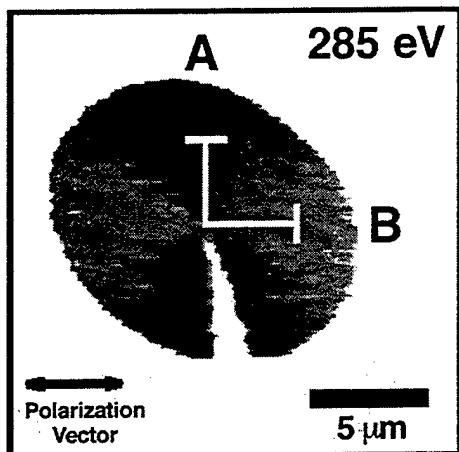




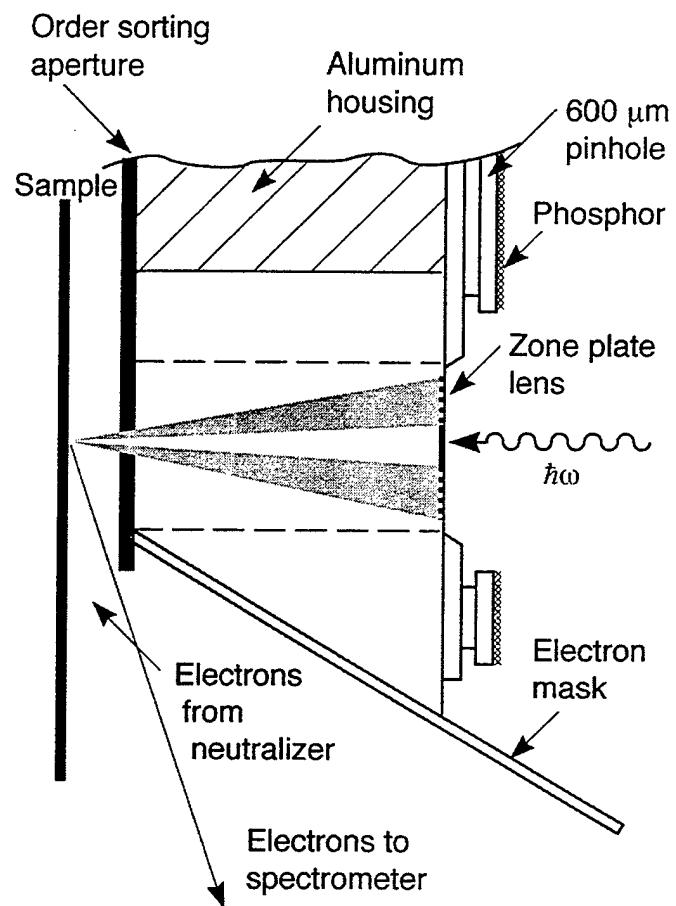
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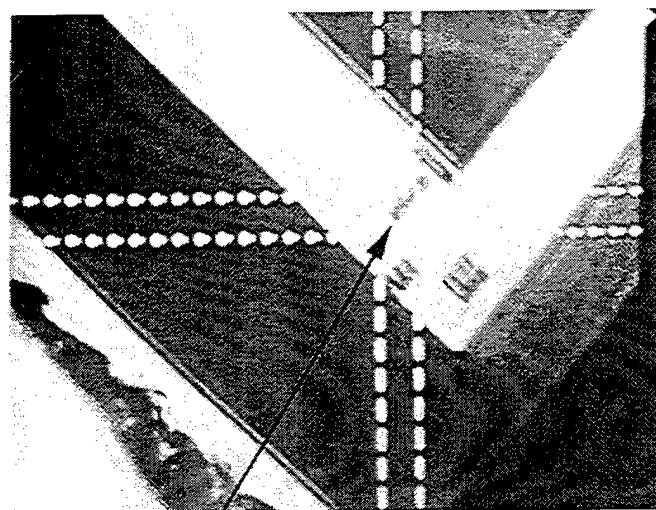
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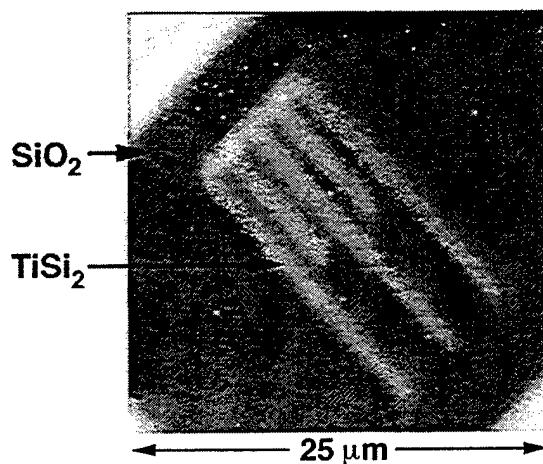
XRD 9707-02770



XBO 9707-02771



100 $\mu\text{m} \times 100 \mu\text{m}$ maximum



XBD 9707-02774

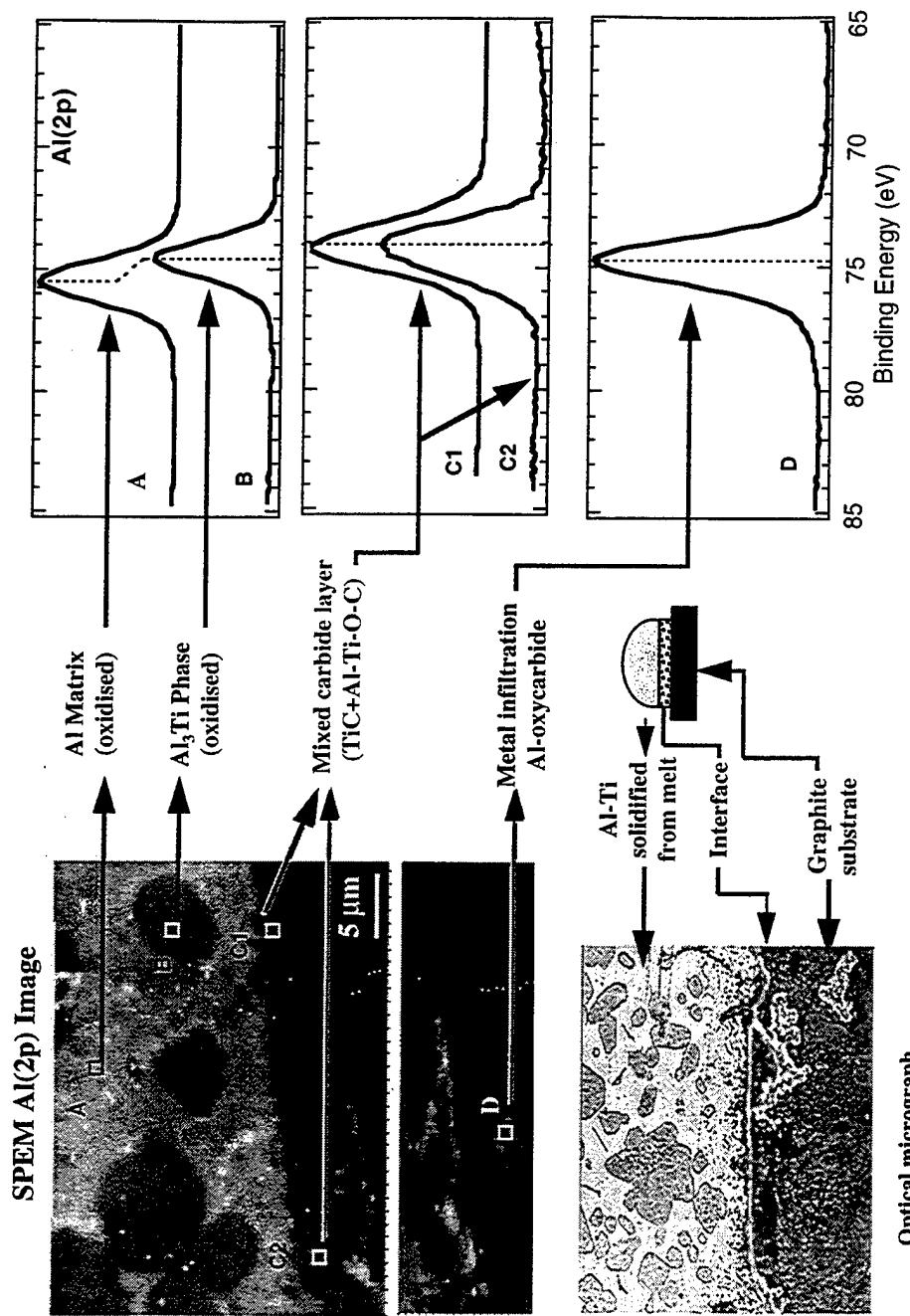


Figure Captions

Figure 1.

The tandem layout of the two microscopes. The upstream microscope is a UHV Scanning PhotoElectron Microscope (SPEM). The photon beam passes through the SPEM chamber to STXM, which is the last item in the beamline.

Figure 2.

Schematic arrangement of the windows, lens, order sorting aperture (OSA), the sample and the detector in STXM.

Figure 3.

The result of a two dimensional x/y scan of the 50micron OSA across the illuminated zone plate. This scan shows a properly illuminated lens and allows the OSA to be accurately positioned.

Figure 4.

A sectioned Kevlar fiber measured in STXM. Absorption spectra are measured at points A and B, showing the dependence on the angle between the photon polarization vector (horizontal) and the radially oriented polymer chains. Spectra are shown for each of the main atomic species present. The polarization contrast reverses between the pi and sigma orbital peaks.

Figure 5.

Schematic arrangement of the lens, order sorting aperture (OSA), the sample and the spectrometer in SPEM.

Figure 6.

Navigation to regions of interest in SPEM can be accomplished by viewing recognizable features on the sample surface with a magnifying telescope and moving the area of interest into the range of the scan stage.

Figure 7.

SPEM images and Al 2p XPS spectra from a metallurgical study of Al/Ti melt interactions with solid graphite. Early results provide quantitative chemical shifts and stoichiometry of alloy precipitates and carbide formation at the interface.

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