APPENDIX

A.1 Introduction to X-ray Spectromicroscopy

The field of soft X-ray spectromicroscopy is relatively new, but expanding rapidly, due to its unique capabilities to address complex problems in materials, environmental, and biological sciences. The essential characteristics of X-ray spectromicroscopy include:

- High spatial resolution - better than 100 nm with a state-of-the-art of ~30 nm.
- Quantitative chemical analysis on a molecular and not just elemental basis, with quantitation based on high resolution X-ray absorption or photoelectron spectroscopy
- Applicable to complex materials including buried and curved interfaces, wet samples (e.g. biological and environmental) and vacuum and radiation sensitive materials.

By combining spectroscopic chemical information with high spatial resolution, X-ray spectro-microscopy provides new research opportunities. These capabilities are best achieved with the high brightness provided by third generation light sources, particularly undulators since other synchrotron source types do not provide the necessary tunability, polarisation control and brightness.

While there are a number of techniques for spatially resolved chemical analysis, they are characterised as either having excellent chemical speciation but inadequate spatial resolution (IR and NMR microscopy), or by having high spatial resolution but inadequate capability for chemical identification (secondary ion microscopy, scanning probe microscopy, Auger, secondary or transmission electron microscopy). Even when they have analytical potential, radiation damage often precludes polymer analysis at high spatial resolution using techniques based on electron or ion impact.

X-PEEM or photoemission electron microscopy using synchrotron x-rays has experienced a similar explosion in application and utility for spatially resolved chemical analysis of surfaces and thin films. While there are quite a few lab-based PEEMs which use work function or shadowing contrast, there are only a handful of synchrotron X-PEEMs, even though the variable photon energy NEXAFS image contrast and microspectroscopy has tremendous chemical analytical capability. In parallel with the zone plate transmission microscope (STXM), we intend to implement an X-PEEM at CLS.

A. 2 X-ray PhotoElectron Emission Microscopy

Photoelectron emission microscopy (PEEM) uses electron optics similar to that found in a scanning electron microscope to image the electron distribution emitted by photoionization of a region (typically 10-100 μm) illuminated by monochromatic light. **Figure 1** is a schematic of a synchrotron based PEEM. PEEM was initially developed using low energy light sources such as a Hg arc lamp and relied mainly on work function variations as the source of contrast. Commercial devices, primarily aimed at the non-synchrotron market, are sold by a number of vendors (Staib, Omicron, Specs). When the light used is tuned X-rays from a synchrotron, the power of X-ray absorption as an analytical tool is introduced. The PEEM x-ray spectromicroscopy method combines x-ray absorption spectroscopy and electron microscopy. The secondary photoelectron intensity (yield) from the sample is used as the signal in the imaging process. Since there is a close relationship (generally linear) between photoelectron yield and the x-ray absorption coefficient, the measured electron yield signal provides not only image contrast but

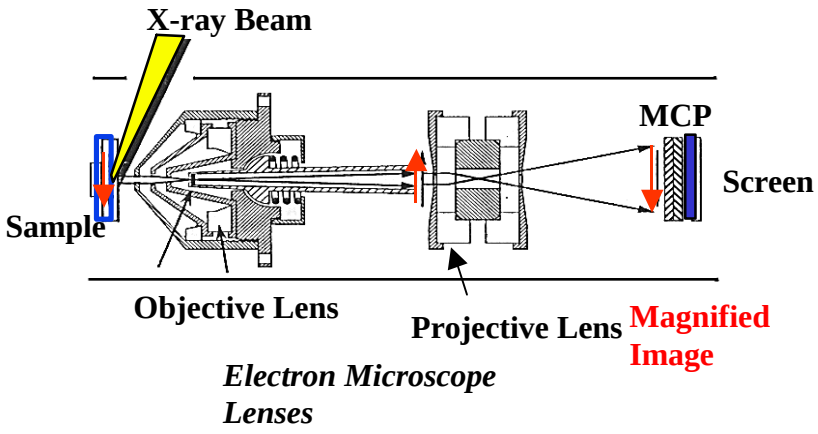
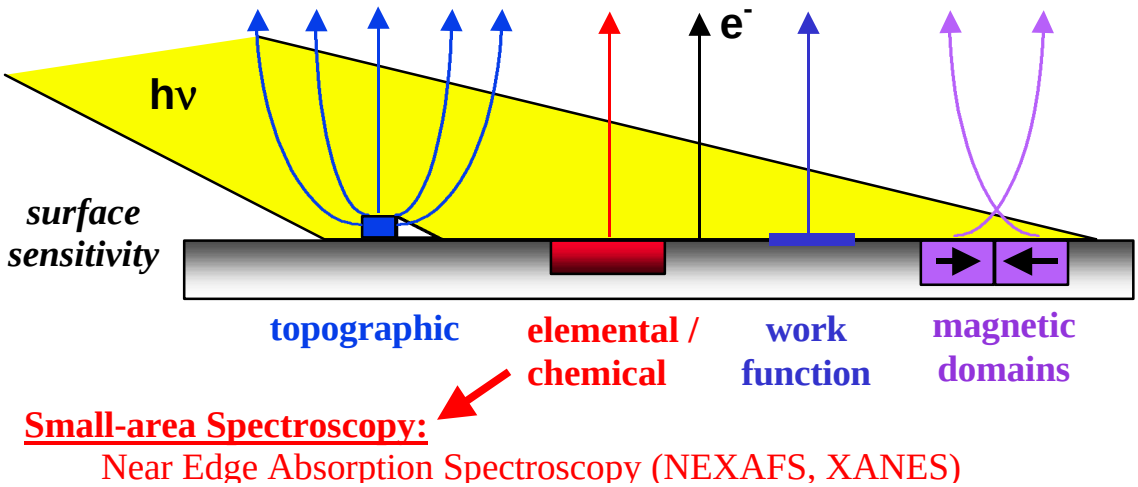


Fig. 1 Schematic of the ALS PEEM (BL 7.3.1, ALS).

spectroscopic information. Information is obtained by tuning the x-ray energy to a particular absorption edge and recording an image ("microscopy" emphasis), by selecting an area in the image and measuring its intensity as a function of photon energy ("spectroscopy" emphasis), or by recording complete image "stacks" as a function of photon energy (spectro-microscopy).

Figure 2 presents the several different contrast mechanisms this method provides: elemental specificity is gained from tuning the x-ray energy to characteristic absorption edges; chemical specificity as well as electronic and structural information is obtained by tuning to specific features in the absorption edge fine structure; bond and charge anisotropies are determined by means of the polarisation dependence (conventional linear dichroism) of near edge absorption resonance; the orientation and size of magnetic moments are probed through magnetic linear and circular dichroism effects of near edge resonances; and finally topographical contrast is obtained by the distortion of the extraction field at surface topographical features.

Fig. 2 Contrast Mechanisms in PhotoElectron Emission Microscopy (PEEM)



High spatial resolution with each contrast mechanism is available by imaging the emitted photo-electrons by means of an electron microscope, typically using an all-electrostatic column. Because of the high extraction fields used in PEEM the technique emphasizes very low energy secondary electrons and thus has a sampling depth of 2-10 nm, much larger than other photo-emission techniques. This is usually an advantage as PEEM is able to probe near surface regions of samples covered by thin protective and/or conducting layers. An example of the results of a recent PEEM experiment carried out at the ALS PEEM 2 is presented in **Figure 3**. In this investigation of protein adsorption on a polymer, it was possible to image the polymer as deposited on a Si wafer both before and after protein adsorption. This is likely a favourable case where the residual conductivity of the aromatic polymer was sufficient to avoid charging artefacts. However similar experiments have been carried out on quite insulating polymer systems by first depositing a very thin (<0.5 nm) metal layer.

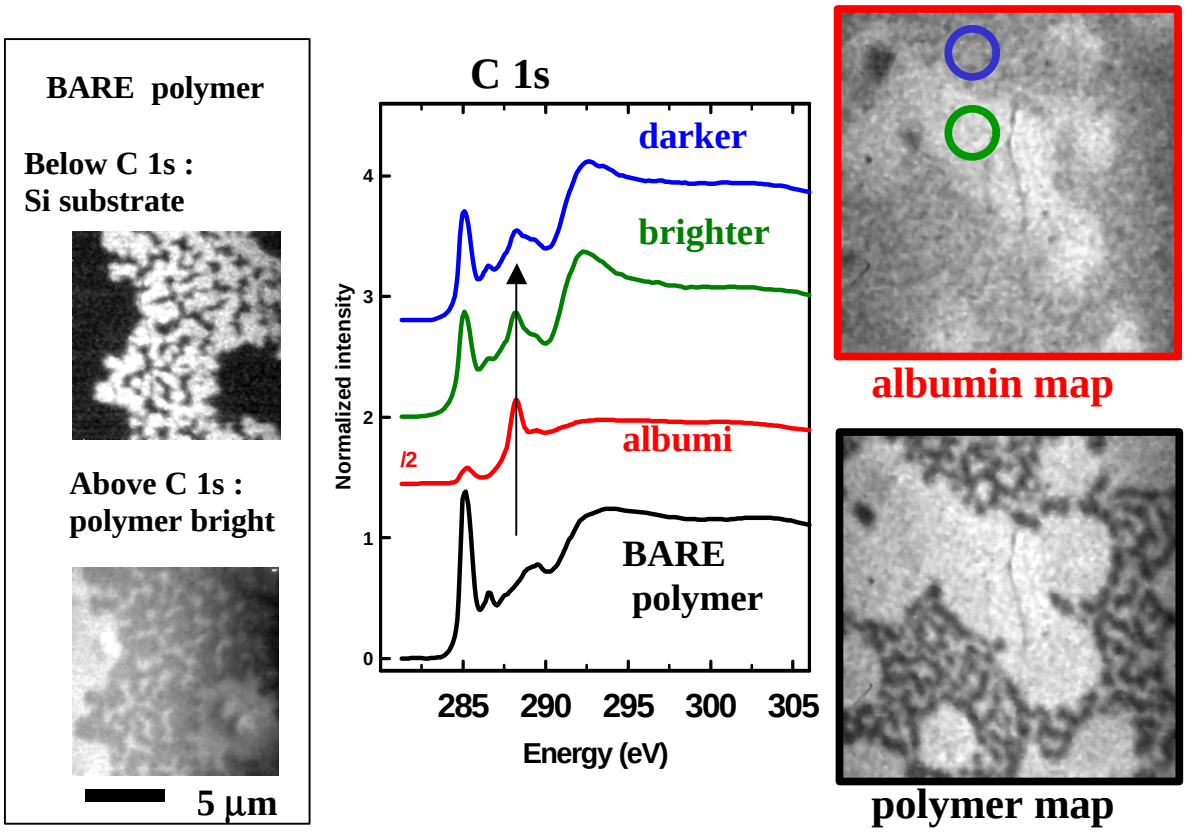


Figure 3 (left) images below (280 eV) and above (300 eV) the C 1s edge. The regions of the Si wafer with low polymer coverage are bright on account of the large photoemission of the underlying Si substrate. Above the C 1s edge the contrast is reduced due to stronger polymer absorption. (centre) spectra of bare and two regions of the protein covered polymer, compared to that of pure human serum albumin (recorded with STXM). (right) example of chemical analysis performed by fitting spectra at each pixel in an image sequence ('stack') from 280-340 eV, to a linear combination of the polymer and protein C 1s NEXAFS spectra. (Work performed by S. Anders, A. Scholl, F. Nolting and A. Hitchcock, ALS BL 7.3.2, July 1999)

1.2 Magnetic Contrast in PEEM microscopy

PEEM microscopy, performed using X-ray Magnetic Linear Dichroism (XMLD) or X-ray Magnetic Circular Dichroism (XMCD) as a contrast mechanism can be sensitive to the surface magnetic structure of materials. With the proposed elliptically polarized undulator (recently endorsed by the facility advisory committee), this PEEM instrument will be particularly powerful for surface microscopy studies. The following references illustrate some of these capabilities.

S. Anders et al, Photoemission electron microscope for the study of magnetic materials, Review-of-Scientific-Instruments. vol.70, no.10; Oct. 1999; p.3973-81.

Principles of X-ray Magnetic Dichroism Spectromicroscopy, J. Stohr et al, Surface Review and Letters, 5 (1998) 1287-1308.

Direct observation of the alignment of ferromagnetic spins by antiferromagnetic spins, F. Nolting et al., Nature 405 (2000) 767-769.

Observation of Antiferromagnetic Domains in Epitaxial Thin Films, A. Scholl et al., *Science* 287 (2000) 1014-1016.