Partial secondary electron-yield NEXAFS spectromicroscopy with an energy-filtered X-PEEM

The narrow energy band pass of an energy-filtered x-ray photoemission electron microscope (X-PEEM) can lead to unusual artifacts when used for spatially resolved near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and imaging of organic surfaces. Work-function differences and the rapid work-function change with radiation exposure can impair quantitative chemical analysis by NEXAFS and invert the expected image contrast. We also find that “partial-yield” detection from the narrow energy band pass of an energy-filtered X-PEEM can lead to distorted NEXAFS spectra. These observations not only are relevant for the analysis of organic surfaces by energy-filtered X-PEEM but also call into question some assumptions about quantitative NEXAFS spectroscopy.

Introduction

X-ray photoemission electron microscopy (X-PEEM) is used by many groups to study “soft” surfaces, such as those associated with bio-adhesion phenomena and the structure of organic thin films [1–3]. X-PEEM can be used to extract near-edge x-ray absorption fine structure (NEXAFS) spectra of the near surface region of a sample (~5 nm deep [4]) with the high lateral spatial resolution of PEEM. NEXAFS spectroscopy provides direct chemical information (elemental composition, chemical bonding and speciation, and molecular orientation measurement) [5] with adequate radiation damage resistance in appropriately executed experiments [4].

The development of energy-filtered PEEM microscopes [6] offers an excellent opportunity to combine photoemission spectromicroscopy [ultraviolet photoemission spectroscopy and x-ray photoemission spectroscopy] of organic thin films with NEXAFS chemical analysis. This combination would be ideal for correlating chemical and structural information with electronic structure for the study of organic electronic materials. This paper describes how energy-filtered X-PEEM can compromise the acquisition of the NEXAFS spectra of some organic materials, in ways that are at times surprising.

Unfiltered PEEM microscopes accept all of the photoelectrons ejected by the sample surface, subject to the 1/E transmission function of the cathode lens—where E refers to the kinetic energy of the photoelectrons. Therefore, low-energy secondary electrons dominate the image intensity. These secondary electrons are created by inelastic scattering of the primary photoelectrons generated by x-ray absorption within the solid. The energy distribution of the ejected secondary electrons reflects the nature of the inelastic scattering processes within the solid [7], as well as the surface work function.

When NEXAFS spectra are recorded in an X-PEEM microscope, electron emission is recorded by the image detector on a pixel-by-pixel basis, as a function of photon energy. This provides a 4-D data set (intensity, x, y, and hv), which can be considered as a NEXAFS spectrum (intensity, hv) for each image pixel (x, y). Here, h is Planck’s constant, and v is frequency. This method is similar to total electron yield detection of the NEXAFS spectra of solids, where a low-current amplifier is used to record the sample drain current as a function of photon energy (current, hv) [8]. This sample current neutralizes the loss of all photoemitted electrons (primary, secondary, etc.) by the sample and is considered to be approximately proportional to the NEXAFS cross section [9]. In comparison, the electron-yield signal in an X-PEEM is modified by the 1/E transmission function of the cathode lens. In an energy-filtered X-PEEM microscope, the energy filter further modifies this electron-yield signal. We describe this detection method as partial secondary...
electron-yield NEXAFS detection, when the secondary emission band is used for NEXAFS spectromicroscopy.

There are several types of energy-filtered PEEM microscopes, with high-pass energy filters based on a retarding mesh [10], and bandpass energy filters based on a single [6] or paired hemispherical analyzers [11], an omega filter [12], or a prism array [13]. The energy filter adds a variable to these X-PEEM experiments, i.e., imaging with a fixed photon energy and a variable electron kinetic energy (intensity, $x$, $y$, $E_{\text{kin}}$, $h\nu$), e.g., photoemission spectromicroscopy, or by imaging with a fixed electron kinetic energy and a variable photon energy (intensity, $x$, $y$, $h\nu$; $E_{\text{kin}}$), e.g., partial-yield NEXAFS spectromicroscopy. This paper focuses on how the bandpass energy filter modifies the NEXAFS signal of organic surfaces, based on our experience with an Elmitec PEEM III microscope with an imaging energy filter [6]. A schematic drawing of this energy-filtered PEEM is shown in Figure 1. Similar phenomena may be observed in a high-pass energy-filtered PEEM, but these effects are not explored in this work.

**Experimental**

Experiments for this work were performed on the Canadian Photoemission Electron Research Spectromicroscope (CaPERS) on various beamlines at the Canadian Light Source (CLS) (VLS-PGM beamline 11ID-2, SGM beamline 11ID-1, spectromicroscopy beamline 10ID-1). Here, VLS-PGM stands for variable line-spacing plane-grating monochromator, and SGM stands for spherical grating monochromator. The CaPERS PEEM microscope is an Elmitec PEEM-III microscope fitted with a hemispherical imaging energy filter [6]. This microscope was operated in a “mobile” mode during the early development of beamlines at the CLS but is now fixed on the PEEM branch of the spectromicroscopy beamline [15].

Samples examined in this work include ultrathin films prepared by Langmuir–Blodgett deposition and spin casting. Phase-separated Langmuir–Blodgett thin films were made from a 2:1 mixture of arachidic acid (AA, $C_{19}H_{39}COOH$) and perfluorotetradecanoic acid (PA, $C_{13}F_{27}COOH$) (2AA:1PA). Full preparation details have been published previously [1, 16]. A thin film (~50–100 nm thick) of polystyrene (polymer source, P2343-St) was prepared by spin casting the polymer dissolved in toluene onto cleaned silicon wafers.

**Experimental results and discussion**

We use X-PEEM microscopy and spectromicroscopy to study the composition and structure of phase-separated organic thin films, such as those prepared by Langmuir–Blodgett deposition [1, 17]. Spatially resolved NEXAFS provides a direct measurement of surface chemical composition and can also provide information on molecular orientation. However, when spatially resolved NEXAFS of surfaces is acquired with an energy-filtered PEEM microscope, the effect of work-function differences on the NEXAFS spectra must be considered.
Figure 2 presents X-PEEM images of a phase-separated Langmuir–Blodgett film formed by a 2 : 1 ratio of arachidic acid (AA) and perfluorodecanoic acid (PA), denoted as 2AA:1PA, at two different energy filter kinetic energy settings. Previous atomic force microscopy and X-PEEM studies have shown that the continuous phase is PA-rich and that the discontinuous phase is AA-rich [1, 16]. The image contrast differences between the left and right images are described here.

**Effect of work-function variation**

Figure 3(a) presents the secondary electron emission spectra of the PA-rich continuous phase and the AA-rich discontinuous phase. These spectra are recorded by illuminating the sample with a fixed photon energy [62 eV for Figure 3(a)] and scanning the kinetic energy of the electrons used to generate the image, in an energy-filtered X-PEEM microscope. This provides, on a pixel-by-pixel basis, the photoemission spectrum of the sample; for low kinetic energy electrons, this provides the secondary electron emission spectrum. Using image-masking techniques, the spectra of all continuous and discontinuous pixels are averaged, and the two spectra are presented here.

It is immediately obvious that the discontinuous phase (AA-rich) emits secondary electrons with a lower kinetic energy than the fluorinated continuous domains (PA-rich). This can be attributed to work-function differences. Alkanethiol self-assembled monolayers are known to decrease the work function of metals such as Ag and Au, whereas perfluorinated alkanethiol self-assembled monolayers will increase the work function of these surfaces [18, 19]. While the structure and formation of the Langmuir–Blodgett films differ, the effect of fluorination on the relative work function is expected to be similar.

The nature of inelastic scattering processes within the AA- and PA-rich domains may also differ, but the energy of electrons that can escape is determined by the work function of each domain.

Figure 2 illustrates how these work-function differences and the secondary electron emission properties affect the energy-filtered X-PEEM image contrast. At lower secondary electron kinetic energies (left image), the lower work-function dispersed AA domains are bright (more photoemission), whereas, at higher secondary electron kinetic energies (right image), the higher work-function...
continuous PA domains are bright. This can be directly correlated with the secondary electron emission spectra in Figure 3(a). Other contrast mechanisms contribute: The thicker AA-rich regions (25 Å thick) will have a stronger NEXAFS cross section than the PA-rich film regions (18 Å thick) [1], but the work-function effects are very strong and will dominate at all x-ray energies. Similar contrast inversion effects have been observed for phase-separated polystyrene/poly(methyl methacrylate) thin films [5].

This work-function contrast is unsurprising, but one must also consider how this phenomenon will affect the quantitative measurement of NEXAFS spectra in an X-PEEM microscope. For example, NEXAFS spectromicroscopy is used to study the localization of protein adsorption on phase-separated polymer surfaces, with unfiltered X-PEEM microscopes [2, 20]. If partial secondary electron-yield NEXAFS spectra are acquired in an energy-filtered X-PEEM microscope at an electron kinetic energy other than the isobestic point, the signal from one phase will be enhanced relative to the signal of the other phase (e.g., signal $\propto$ NEXAFS cross section $\times$ secondary electron emission propensity). Therefore, the signal is no longer directly proportional to the chemical composition. For complex organic surfaces, it is not easily possible to know the work-function variation in advance of the experiment.

**Time stability of surface work function**

Our results also indicate that the work function of organic thin films is not stable in time. Figure 3(b) presents the secondary electron emission spectra of AA-rich domains in a phase-separated 2AA:1PA Langmuir–Blodgett thin film as a function of dose; these traces are acquired from the same sample area, in sequence. We observe that the secondary electron emission band shifts to higher energy with sample exposure, converging after a few scans. The initial changes are quite rapid. It appears that photon illumination increases the work function of the sample. We note that the initial state of the sample surface is not pristine: these Langmuir–Blodgett films are prepared on a water surface and transferred and stored in air. These rapid work function changes could be attributed to desorption of species from the surface with radiation exposure.

Partial secondary electron-yield NEXAFS spectra of organic surfaces recorded with an energy-filtered PEEM can be unstable as the secondary emission rapidly changes during the initial exposure. This effect is not necessarily limited to NEXAFS acquired in an X-PEEM microscope. We have previously observed that the first NEXAFS scan of an organic sample, which is recorded by a sample current total electron yield, often has a higher background than subsequent scans. This observation is consistent to a rapid increase in work function with initial radiation exposure. A comparison to pristine in vacuo prepared organic samples and photon-stimulated desorption studies would be needed to properly characterize this effect.

**Partial secondary electron-yield NEXAFS detection**

We have seen unusual effects in the partial secondary electron-yield NEXAFS spectra of organic thin films when recorded by energy-filtered PEEM microscopy. We find that the NEXAFS spectrum of the organic surfaces differs when recorded at different secondary electron emission energies. To explore this effect, we have recorded the secondary electron emission spectrum, in dispersion mode, for a series of bins identified in panel (a). NEXAFS spectra are not normalized for the $I_o$ flux, where $I_o$ is the incident photon flux.
It is immediately obvious that the shape of the NEXAFS spectra differs when extracted from different secondary electron-yield bins; the Carbon 1s $\rightarrow \pi^*(C=C)$ transition at 285 eV in the NEXAFS spectra extracted from low electron kinetic energy bins (1, 2, and 3) is considerably sharper than that from higher bins. The higher energy bins (6–10) show dispersion from a valence photoemission peak that shifts to higher energy as a function of photon energy.

Upon close examination of the secondary emission spectrum [Figure 4(b)], we observe that the secondary electron emission shifts to lower energy at the Carbon 1s $\rightarrow \pi^*(C=C)$ transition energy (285 eV). When this electron emission band shifts to lower kinetic energy, the signal level in the low energy bins (1–3) increases, and the intensity of the Carbon 1s $\rightarrow \pi^*(C=C)$ transition is artificially enhanced. Identical effects are observed in subsequent scans of the same sample region; this effect is not associated with radiation damage.

It appears as if the sample work function changes with strong photon absorption and photon energy. As the secondary electron emission onset energy decreases, more secondary electrons escape into the low-energy channels, distorting the strength of strongly absorbing features. This effect appears to be related to the x-ray absorption cross section; the secondary electron emission band is also shifted to higher energy with 330-eV x-ray illumination, where polystyrene also absorbs strongly but not as strong as at 285 eV.

The origin of this effect is not clear, as sample charging should have the opposite effect than observed. A nonconductive sample will tend to become more positively charged when it absorbs x-rays and photoelectrons are ejected. This positive charge should retard the emission of low-energy electrons, shifting the onset of the secondary electron emission spectrum to higher energy, not lower.

This partial secondary electron-yield effect has been seen in a series of similar experiments on energy-filtered X-PEEM, but the secondary electron emission shift was only observed when the energy analyzer dispersion function was measured as a function of photon energy. The shifting higher energy peaks in Figure 4(d) also illustrates that a primary photoelectron band from valence photoemission is superimposed on the partial secondary electron emission spectra. Depending on the magnitude of the apparent work-function shift or valence photoemission contribution, the energy filter can distort the shape of NEXAFS spectra of organic surfaces.

**Conclusion**
Results have shown that one must use caution when measuring NEXAFS spectra of organic thin films in an energy-filtered X-PEEM. Observations have also suggested the need for concern in traditional total electron-yield NEXAFS analysis. As lower work-function samples will have a stronger electron-yield signal, quantitative analysis of materials with greatly different work functions—or an unstable work function—should be questioned. The origin of the apparent shift in work function with strong photon absorption is unknown and deserves further study.

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## References


