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Photoelectron Emission Microscopy and Its Application to the Study of Polymer Surfaces

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Photoelectron emission microscopy and its application to the study of polymer surfaces

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The X-ray Photoelectron Emission Microscopy (X-PEEM) at the Advanced Light Source (ALS) has a spatial resolution of 0.2 microns at an accelerating voltage of 12kV. The tunability of the photon energy is used to provide chemical state information using near edge X-ray absorption fine structure (NEXAFS) spectroscopy on the sub-micrometer scale.

The homogeneity of thin films of polymer blends was studied for various film thicknesses. The polystyrene/polyvinylmethylether film of 194 Å showed protrusions of 2-3 μm diameter with an enriched polystyrene content while the polystyrene/polystyreneacrylonitrile 504 Å thick films showed 5-6 μm segregated regions without any topological structure.

Introduction

After the first photoelectron images taken by Brücke [1] in 1933 interest in the photoemission imaging technique increased dramatically when the UHV technology allowed the study of clean surfaces. The use of synchrotron light as the excitation source further opened the possibilities to develop the so called X-ray Photoelectron Emission

Microscope (X-PEEM) [2-4] based on the NEXAFS [5] technique to obtain spectroscopic information on a sub-micron scale.

Here we present a study of phase segregation in thin films of polymer binary mixtures with X-PEEM. Phase segregation in polymer thin film mixtures confined between two surfaces has been the focus of much recent research ref. [6-8]. The roughening at vacuum/polymer interface above the critical solution temperature of polymer blends was reported by Slawecki et al. [9] where they probed the topography and elasticity of the sample surfaces using variety of surface sensitive techniques, including scanning probe microscopy (AFM) and static secondary ion mass spectrometry. The correlation between the topography and polymer compositions were extracted indirectly from the friction and elasticity measurement with scanning probe microscopy. No measurements were performed to probe the morphology and at the same time detect the chemical composition of the surface. The advantage of X-PEEM is that it can map both topography and chemical compositions of surfaces of polymer films with sub-micron lateral resolution and with exceptional surface depth sensitivity (10 nm). Further more, X-PEEM has much lower radiation damage to the polymer thin films in comparison with other electron microscopy techniques. This is shown in the study of phase separated polymer blends by Ade et al. [10]. Therefore, X-PEEM provide us a powerful tool for studying phase segregation of polymer thin films with capability to correlate the surface morphology and the polymer phase compositions. In this paper, we report the study of phase segregation in a thin film of PS/PVME mixture, using X-PEEM to obtain combined topological and NEXAFS spectra, and the investigation of PS/PSAN thin films using element specificity of NEXAFS.

X-PEEM

The instrument used at the Advanced Light Source was built in the group of Tonner [3, 4, 11] The optical system is designed on the basis of the tabulated properties of unipotential lenses measured by G. Rempfer [12] and consists of two electrostatic lenses, an accelerating objective and a projective lens giving a combined maximum magnification factor of 1000. Resolution tests were carried out on Cu patterns deposited on a Si oxidized wafer using the 10%/90% knife edge resolution criteria. For an accelerating voltage of 12 kV the resolution was 0.2 µm, limited primarily by the chromatic and spherical aberration of the accelerating field.

Polymers blends

Two types of binary polymers blend thin films were produced by spin coating a toluene solution onto HF etched Si substrates and annealing for 3 hours at 170 °C in $1*10^{-6}$ Pa to prevent oxidative degradation. The thickness of the films was determined by ellipsometry. The X-PEEM measurements were taken on the undulator Beamline 7.0 at the ALS [13]. The photon flux on the sample was maintained below $4*10^{11}$photons/s (spot size 100*100 µm) in order to minimize degradation of the polymers. The spectral resolution at 300 eV was $\delta E=0.1$ eV.

The first sample was a 194 Å thick film of a mixture of 15% polystyrene (PS of Mw=96,000 and Mw/Mn=1.04) and 85% polyvinylmethylether (PVME of Mw= 84,000 and Mw/Mn=1.40). Only the polystyrene polymer has benzene rings. The NEXAFS carbon K edge absorption spectra of polystyrene shows a π^* resonances at 285 eV [5] characteristic of the C=C bonds in the benzene ring. An X-PEEM image taken at a photon energy of 270 eV is shown in fig. 1. Dark spots are 2-3 µm diameter. A better understanding of the information contained in fig. 1 is obtained by collecting NEXAFS spectra within four different regions of this sample. Regions 1 and 2 are defined inside the dark spots and regions 3 and 4 are in the surrounding bright region. In fig. 2a we have plotted the corresponding absorption spectra at the carbon K edge. At 270 eV most of the signal originates from the substrate Si $L_{2,3}$ edge. Thus the observed contrast is due to variation in thickness of the coating with the bright regions corresponding to presence of thinner coating. The darks spots correspond to protrusions. Such protrusions were also observed on similar blends by Slawecki et al. [9] by means of atomic force microscopy. They reported an enriched concentration of PS within the protrusions. We confirm their findings by analyzing the normalized NEXAFS [5] spectra in fig.2b. Both regions (protrusions and surrounding) contains some PS as indicated by the presence of the π^* resonance, but the concentration ratio of PS over PVME is higher within the protrusions as the ratio of the π^* over σ^* resonance is higher. The formation of the PS enriched protrusions during the annealing process is *not* accompanied by a total dewetting of blend in the region surrounding the protrusions. This example illustrates the possibility to obtain a topological information combined with the chemical distribution in the phase segregation of PS/PVME blends.

The second sample was a 504 Å thick film composed of 50% polystyrene (PS of Mw=96,000 and Mw/Mn=1.04) with 50 % of polystyrene-polyacrylonitrile (PSAN of Mw=152,100 and Mw/Mn=2.03) diblock copolymer. The weight percentage of the PS and PAN in the PSAN copolymer is 75% and 25 % respectively. PSAN is differentiated from PS by the presence of a N≡O along the polymeric chain. An image of this blend obtained at the nitrogen K edge (400.5 eV) is displayed in fig. 3a showing some brighter regions of about 5-6 μm diameter. The NEXAFS spectra taken within these brighter regions (reg.1 and 2 on the picture) are displayed in fig. 3b, confirming indeed the presence of nitrogen. In this case the X-PEEM analysis is sensitive to a pure chemical contrast. No domains were distinguished below the nitrogen K edge. Other blends of PS/PVME and PS/PSAN of thickness 30 Å were studied in the same way. We could not distinguish any sign of topological nor chemical segregation within our resolution limit.

A low intensity of the nitrogen K edge absorption peak compared to the background signal in Fig. 3b is due to radiation damage of the sample. In order to perform micro-NEXAFS studies on very sensitive materials such as polymers, one has to work at very low X-ray intensities. To improve the signal to noise ratio in the images the design of the microscope optics must be optimized to maximize its electron transmission function. To achieve a high electron transmission simultaneously with a high spatial resolution, our new X-PEEM will include an electrostatic hyperbolic electron mirror [14] to correct the chromatic and spherical aberration of the electrostatic lenses and of the accelerating field between the sample and the objective. In addition it will work at substantially higher voltage (30 kV) and use a much more efficient YAG-cooled CCD detector instead of the present channel plate/phosphor/CCD combination currently used.

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Figures Captions

Fig. 1: Image of a 194 Å thick blend of 15% PS + 85% PMVE recorded at 270 eV. Field of view 60 µm.

Fig. 2: NEXAFS carbon K edge absorption spectra recorded in the regions 1 to 4 defined on fig. 1. In (a) the spectra are displayed as recorded without any normalization while in (b) a constant background was subtracted below the absorption edge and they are normalized at 340 eV to get the signal per atoms. In fig. 2b both signals of reg. 1+2 from the dark spots (protrusions) and both signal from the surrounding reg. 3+4 have been averaged.

Fig. 3: a) Image of a 504 Å thick blend of 50% PS + 50% PSAN recorded at 400.5eV. Field of view 60 µm. The two black spots on the right side of the image correspond to burned channels of the multichannel plate image intensifier. b) NEXAFS nitrogen K edge absorption spectra recorded in the regions 1 to 4 defined on fig. 3a. Spectra not normalized and rigidly shifted along the intensity axis.

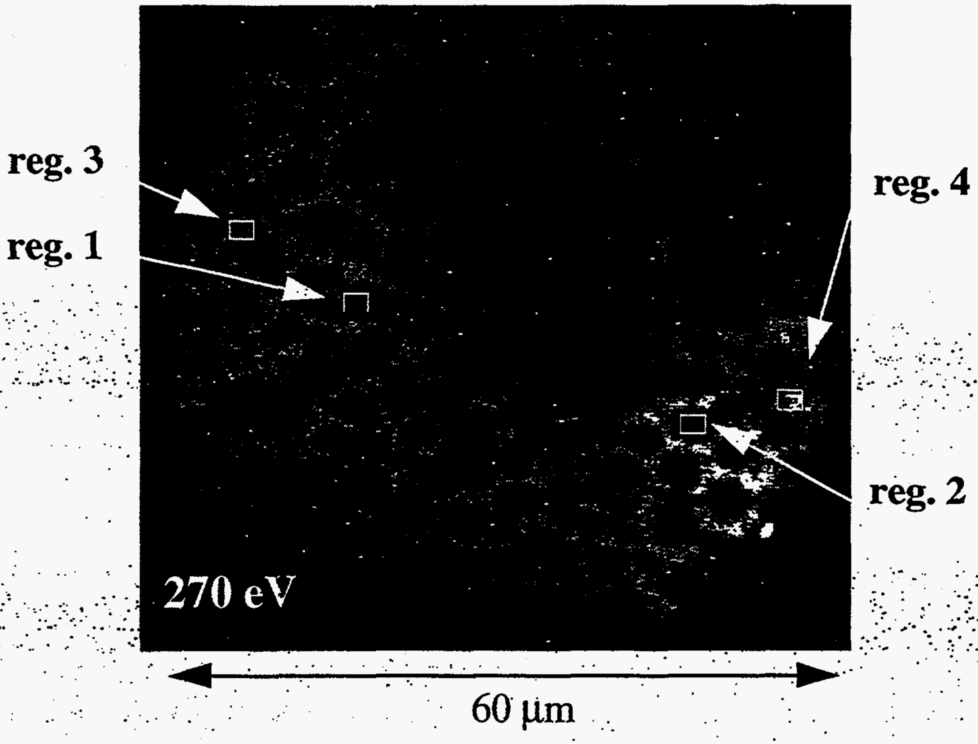

Figure 1

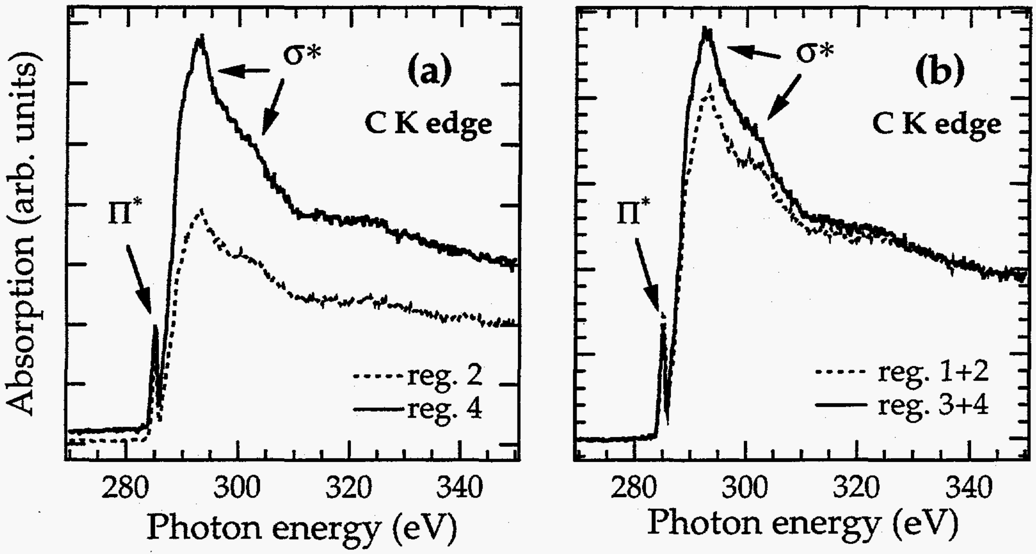
Absorption (arb. units)
Photon energy (eV)
280
300
320
340
(a)
C K edge
σ*
Π*
reg. 2
reg. 4
(b)
C K edge
σ*
Π*
reg. 1+2
reg. 3+4

Figure 2

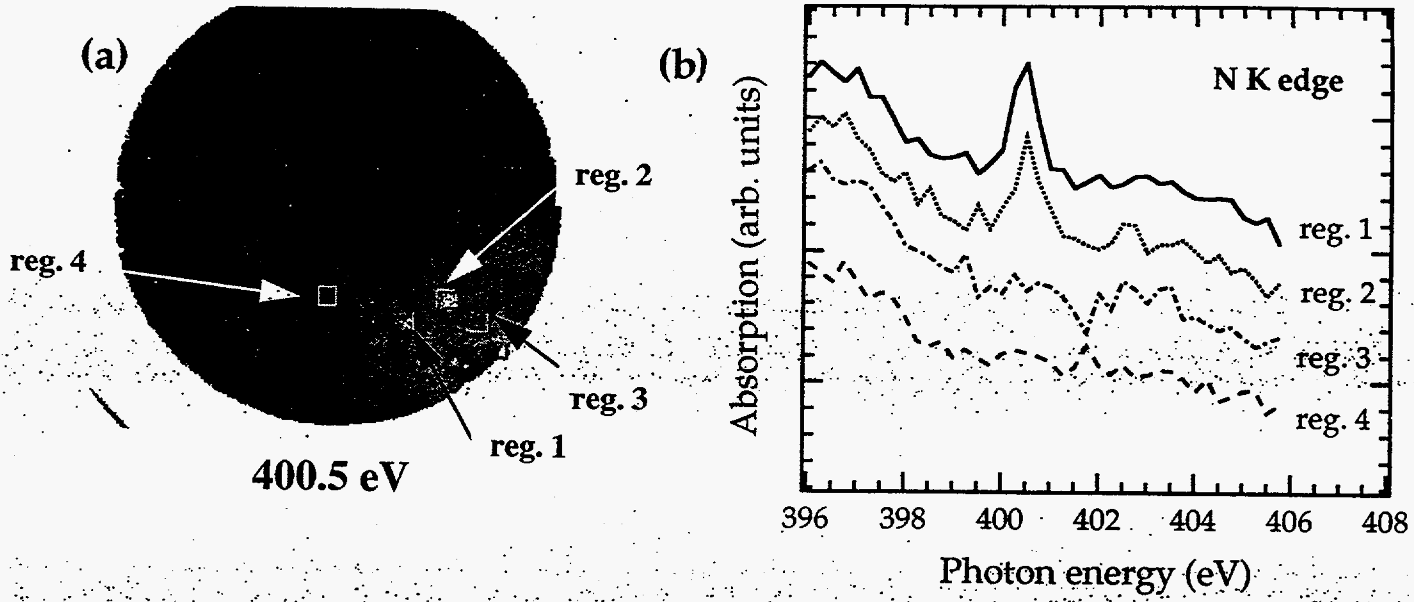
(a)
reg. 2
reg. 4
reg. 3
reg. 1
400.5 eV
(b)
N K edge
Absorption (arb. units)
reg. 1
reg. 2
reg. 3
reg. 4
396
398
400
402
404
406
408
Photon energy (eV)

Figure 3