

X-ray absorption spectroscopy to probe interfacial issues in photolithography

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ABSTRACT

We utilize near edge X-ray absorption fine structure spectroscopy (NEXAFS) to provide detailed chemical insight into two interfacial problems facing sub-100 nm patterning. First, chemically amplified photo-resists are sensitive to surface phenomenon, which causes deviations in the pattern profile near the interface. Striking examples include T-topping, closure, footing, and undercutting. NEXAFS was used to examine surface segregation of a photo-acid generator at the resist/air interface and to illustrate that the surface extent of deprotection in a model resist film can be different than the bulk extent of deprotection. Second, line edge roughness becomes increasingly critical with shrinking patterns, and may be intimately related to the line edge deprotection profile. A NEXAFS technique to surface depth profile for compositional gradients is described with the potential to provide chemical information about the resist line edge.

1. INTRODUCTION

Control of the shape, critical dimension (CD), and line edge roughness (LER) is essential for the fabrication of sub-100 nm features, where the CD and roughness budget are approaching the molecular dimension of the resist polymers¹. Many factors can impact both CD and LER, including segregation of the photo-acid generator (PAG) molecules or resist additives², photo-generated acid diffusion³, out gassing of photo-resist materials⁴, film thickness effects⁵, and copolymer composition and phase separation between protected and de-protected polymers at the interface between exposed and unexposed areas⁶. Due to the complexity of lithographic processing, processing parameters such as bake temperature, bake time, exposure dose, etc. must be optimized to control CD⁷.

In addition to these factors, with shrinking pattern sizes the performance of chemically amplified photo-resists will become increasingly prone to surface phenomena, which cause deviations in the pattern profile near the interface. Commonly observed problems include T-topping, closure, footing, and undercutting⁸. Many chemically amplified resists exhibit a dramatic degradation in the lithographic performance due to airborne contamination. Resist contaminants and airborne amines have been shown to induce a thin base insoluble skin on the resist surface leading to T-topping or closure⁹⁻¹³. Air purification systems and the application of a protective “base neutralizing” overcoat on the resists have been used to prevent contamination and to eliminate t-topping and closure^{10,13}. Segregation or depletion of resist components such as a PAG, dissolution inhibitor, or base additives at interfaces is also a potential cause of T-topping. For example, a lower PAG concentration at the resist/air interface could lead to slower deprotection kinetics and possibly incomplete deprotection. Segregation of the dissolution inhibitor to the interface could slow the surface dissolution rate. PAG size was shown to influence T-topping behavior supposedly by increasing the hydrophobic character of the resist resulting in an increase in surface inhibition¹⁴.

Line edge roughness (LER) is an interfacial problem that can become prevalent with decreasing feature size. LER that is acceptable for current patterning dimensions will be unacceptable in smaller patterns. The push to reduce features dimensions to sub-100 nm levels (where dimension tolerances are typically 1 % to 5 %) requires LER control on nanometer length scales¹. This is a daunting challenge since these length scales are similar to the dimensions of the resist polymer molecules themselves. In addition to effects from image projection^{15,16}, material

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factors such as acid diffusion / reaction front propagation¹⁷⁻¹⁹, resist chemistry²⁰, and dissolution behavior²¹ can contribute to LER.

Due to the complex interfacial problems that can impact the shape, size, and roughness of sub-100 nm patterning, it is important to develop and utilize new tools to probe the interfacial composition and structure of photoresist films. Here we demonstrate the utility of NEXAFS for providing information about lithographic interfaces. First, focus is placed on the T-topping / closure issue by probing the extent of deprotection at the resist surface. Second, a NEXAFS technique is described to extract surface composition profiles in a model line edge region, offering the potential to provide detailed chemical information about compositional gradients in lithographic patterns.

2. EXPERIMENTAL²²

2.1 Materials and methods

The model resist solution was composed of 0.7 g of protected polymer poly(tertbutyloxy- carbonyloxy- styrene, $M_{n,r}=15,000$) (PBOCSt) mixed with 0.035 g (0.05 mass fraction of PFOS relative to the polymer) of the PAG, bis(p-tert-butylphenyl) iodonium perfluorooctanesulfonate (PFOS). This mixture was dissolved in 20 mL of propylene glycol methyl ether acetate (PGMEA). The resist solution was spun cast onto silicon wafers at 1500 rpm for 60 s and then post apply baked (PAB) for 60 s at 100 °C. The PBOCSt / PFOS films were blanket exposed to ultra-violet radiation from a broadband source with wavelengths ranging between (220 and 260) nm with a total dose of 500 mJ/cm². After exposure the films were post exposure baked (PEB) at 100 °C. Polyhydroxystyrene, $M_{n,r}=5,000$, (PHS) / PFOS, and polystyrene, $M_{n,r}=24,000$, (PS) / PFOS films were made according to the same procedures described above.

2.2 Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

NEXAFS measurements were conducted at the U7A beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. A monochromator with 600 line/mm grating, providing ± 0.15 eV resolution, was used for all the NEXAFS spectra. The monochromator energy scale was calibrated by the carbon K-edge π^* transition of graphite at 285.35 eV. All the spectra were recorded at room temperature in the NIST – Dow material characterization chamber²³ at 10^{-6} Pa. The spectra were normalized to the incident beam intensity, I_0 , by collecting the total electron yield intensity from a gold coated 90 % transmitting grid placed in the incoming X-ray beam path. The carbon fluorescence-yield intensity was measured utilizing a differentially pumped, UHV compatible proportional counter filled with 0.27 MPa of P-90 (90 % methane, 10 % argon) in an energy dispersive mode²⁹ to reduce background fluorescence from other elements. Surface sensitive partial electron yield measurements were made (probe depth of approximately (1 nm to 6 nm) by applying a negative bias on the entrance grid of the channeltron electron detector. For the carbon K-edge spectra (260 to 330) eV and the oxygen K-edge spectra (510 to 570) eV, the electron yield detector was set with a negative bias of 150 eV and 320 eV respectively. The spectra were collected with the incident beam at the magic angle (54.7°) relative to the sample in order to remove any polarization dependence. For the NEXAFS spectra in this paper the experimental standard uncertainty in the peak position is similar to the grating resolution of ± 0.15 eV. The relative uncertainty in the NEXAFS intensity is less than $\pm 5\%$ and was determined by multiple scans on a sample. For some experiments, bilayer samples of PBOCSt and PHS were spun cast onto silicon wafers. The wafers were cleaned by immersion in sulfuric acid and hydrogen peroxide solution followed by a rinse in deionized water. A hydrophobic surface was generated by treating the wafers with hexamethyldisilazane (HMDS) vapor in a vacuum oven. The bottom PBOCSt layer was spun cast from solution with PGMEA and soft baked for 60 s at 130 °C. A top layer of PHS (with a 5 % mass fraction of PFOS) was spun cast on PBOCSt from a solution of n-butanol. The samples were exposed to UV radiation, and post exposure baked for various times at 90 °C. After PEB, the soluble top portion of the bilayer film was removed (developed) by immersion in aqueous 0.26 N tetra-methyl-ammonium-hydroxide solution. NEXAFS measurements were then conducted on the developed bilayer samples as a function of the electron yield detector bias. For the depth profiling measurements on the bilayer surfaces the negative bias on the electron yield detector was varied between (50 and 245) eV.

3. RESULTS AND DISCUSSION

3.1 NEXAFS at the resist/air interface

Figure 1 shows a schematic depicting the principles of NEXAFS. The sample is exposed to tunable plane polarized, monochromatic X-ray radiation from a synchrotron light source. In these experiments, the incident radiation is scanned over the carbon K-edge region, an energy range from (260 to 330) eV. X-rays are preferentially absorbed by the sample when the incident radiation is at the appropriate energy to allow the excitation of a core shell electron to an unoccupied molecular orbital. During electronic relaxation Auger electrons and characteristic fluorescence photons are released. The electronic relaxation processes may release more than one electron. These electrons can only escape from the top surface of the sample (1 to 10) nm. The photons are detected from approximately 100 nm within the sample. NEXAFS has elemental sensitivity because the characteristic binding energies, carbon, nitrogen, oxygen, and fluorine core electrons are well separated in energy. In addition, due to the well-defined energy gap associated with a core shell / unoccupied orbital transition, NEXAFS is also sensitive to the bonding characteristics of the atom²⁵.

Figure 1 also shows a carbon edge electron yield NEXAFS spectrum for PBOCSt. In the pre-edge region, the incident radiation is weakly absorbed by the sample. The intensity in this region, I_b , is the background signal (often from the substrate and sample, lower energy absorption edges, orbital transitions other than core level transitions, etc.). Above the carbon K edge (285 eV), the signal intensity (electron or fluorescence yield) increases when the incident radiation is strongly adsorbed by the sample. In the near edge region, the peaks represent chemical bonding structure in the sample because the emission signal increases when the incident energy is the appropriate energy to cause an electron transition from the core 1s orbital to an unoccupied molecular orbital. The absorption edge represents the ionization of the core shell electron to the continuum. The edge jump, I_j , is defined as $I_s - I_b$. In the post edge region the signal intensity, I_j , represents total amount of carbon (since the scan is over the carbon K-edge energy range) in the sampling volume. All the NEXAFS spectra in this paper are pre-edge jump normalized to zero, by subtracting I_b from the spectrum. Notice the well - defined peaks in the near edge region. This is a consequence of the synchrotron light source, which has high enough intensity to filter the incident radiation. The monochromatic excitation therefore allows for high resolution of the chemical peaks.

Figure 2 shows the carbon edge NEXAFS spectra for the neat components used in our model resist system. The spectra are vertically offset for clarity. The top spectrum is for the protected polymer, PBOCSt. The peak at 285.0 eV reflects the π^* transition from the carbon-carbon double bonds in the styrene ring. At 290.3 eV is a peak associated with the protective group, specifically the π^* transition of the carbon-oxygen double bond from the carbonyl group. The middle spectrum, for the PFOS PAG, also displays a sharp carbon-carbon π^* transition similar to PBOCSt. However, the broad peaks between (292.0 and 298.0) eV are due to σ^* transitions for carbon-fluorine bonds (292.0 and 298.0) eV and carbon-carbon bonds, 295.0 eV, on PFOS. The bottom spectrum is for the deprotected polymer, PHS, which also contains the strong π^* transition at 285.0 eV. Distinct peaks can be used to detect the individual resist components. For example, the peak at 290.3 eV in PBOCSt, associated with the protective group, is not present in PHS or PFOS, allowing the direct monitoring of the de-protection reaction. Also the carbon-fluorine peaks in PFOS are not present in the other two spectra, although they may partially overlap with the carbon-carbon σ^* transition.

Figure 3 shows the electron yield spectrum for the carbon K-edge of a PBOCSt / PFOS sample with PFOS mass fraction of 0.05 (solid line). The carbon-fluorine σ^* peaks (at 292.0 eV and 298.0 eV) from the PFOS are clearly visible as well as the π^* transition associated with the carbonyl on PBOCSt (290.3 eV) and the carbon-carbon double bonds on the ring (285.0 eV). Using the pure component electron yield spectra from Figure 2, the measured electron yield spectra for the PBOCSt / PFOS film (solid line) in Figure 3 can be adequately fit with a linear combination (dotted line) of 0.4 times the pure PFOS spectrum and 0.6 times the pure PBOCSt spectrum. The inset shows the fluorescence yield (bulk) spectrum for the PBOCSt / PFOS sample. The carbon-fluorine σ^* peaks associated with the PFOS were not detected in the fluorescence yield spectrum, suggesting a significantly lower PFOS concentration in the bulk film relative to the film surface.

A PBOCSt / PFOS mixture with 0.05 PFOS mass fraction corresponds to a PFOS mole fraction of 0.013 relative to the moles of PBOCSt monomers. The linear spectral combination (shown in Figure 3) can be used to extract the surface mole fraction of PFOS, but must be corrected to account for the carbon density in the PFOS molecules relative to the PBOCSt monomers. This relative carbon density was estimated from the ratio of the carbon edge jump of PBOCSt relative to PFOS in the pre-edge jump normalized spectrum for the neat components.

For example, the edge jump intensity (I_j defined in Figure 1 in arbitrary units) for PBOCSt was 1.17 and for PFOS was 0.41. The linear combination in Figure 3 gives 0.4/0.6 as the ratio of carbon signal from PFOS relative to carbon signal from PBOCSt. Converting the linear combination to a mole fraction ratio requires normalizing with the carbon content in PBOCSt relative to PFOS (1.17/0.41). This conversion gives a value of $(0.4/0.6)(1.17/0.41)=1.9$ for the moles of PFOS per mole of PBOCSt monomers, yielding a PFOS surface mole fraction of $0.65=1.9/(1.9+1)$. The primary uncertainty associated with measuring the PFOS surface mole fraction is due to fitting the measured spectra for the polymer / PFOS films by a linear combination of the pure component spectra. The linear combinations provided an adequate fit with a relative standard uncertainty of ± 0.05 for the fraction of each pure component spectra used. This translated to a relative uncertainty in the surface PFOS mole fraction ranging from (0.04 to 0.07).

Figure 4 plots the surface mole fraction of PFOS (calculated from the NEXAFS electron yield spectra via the linear combination described in Figure 3) versus the bulk PFOS mole fraction (calculated from mass measurements in the spin casting formulation). For PBOCSt, PHS, and PS the surface mole fraction of PFOS is much larger than the bulk. However, the amount of surface segregation is polymer dependent, with larger surface segregation of PFOS in the non-polar PBOCSt, and PS polymers. With PS and PBOCSt, the surface mole fraction of PFOS is (50 to 70) times the bulk fraction. With PHS the surface mole fraction is approximately 20 times the bulk value. The error bars in Figure 4 represent the relative standard uncertainty in the surface mole fraction. The inset in Figure 3 shows the fluorescence yield carbon K-edge spectrum for the PBOCSt / PFOS film. Carbon-fluorine peaks are observed in the carbon K-edge electron yield spectrum but not observed in the carbon K-edge fluorescence yield spectrum, qualitatively verifying the PFOS surface enrichment. If the surface PFOS content were similar to the bulk value (0.05 mass fraction or 0.013 mole fraction), the carbon-fluorine σ^* peaks would not be observed in the carbon edge electron yield spectra because the carbon-fluorine σ^* contribution from PFOS would be dominated by a large carbon background from the PBOCSt fraction. The fact that the carbon-fluorine peaks can be observed strongly in the carbon edge electron yield spectrum qualitatively illustrates a significant PFOS segregation to the film surface. The carbon-fluorine σ^* peaks were also observed in the carbon edge electron yield spectra but not in the fluorescence yield spectra for PHS / PFOS and PS / PFOS films. It is surprising that the fluorinated PFOS exhibits more surface segregation in the non-polar polymers (PS and PBOCSt) than in the polar polymer PHS, as one might expect more surface segregation of a fluorinated component to the higher energy surface of a polar polymer. However, PFOS is also an ionic species (see structure in Figure 2). It is possible that a competition exist between the drive to lower the surface energy by segregation of fluorinated groups to the air interface, and strong ionic – dipole interactions between the PFOS and the polar polymer in the bulk of the film. With a non-polar polymer, the surface energy effect dominates leading to high concentrations of PFOS at the interface. With the polar polymer, the ionic – dipolar interactions between PHS and PFOS in the bulk film become important, leading to less surface segregation. To test this hypothesis, we are currently investigating the influence of different types of PAGs on surface segregation.

Figure 5 compares the electron and fluorescence yield for the PBOCSt / PFOS films after various processing conditions. By monitoring the C=O π^* transition from the carbonyl on PBOCSt, the extent of deprotection can be followed during processing. In Figure 5 the spectra are both pre and post edge jump normalized. The post edge jump normalization involves dividing the pre-edge jump normalized spectra by the edge jump intensity (I_j from Figure 1). This eliminates the spectral dependence on total carbon content in the sampling volume, thus changes in the NEXAFS peak intensity are due to chemical changes in the system. The films in Figure 5 were treated with typical resist processing conditions including; post apply bake (PAB) for 60 s at 100 °C; UV exposure 500 mJ/cm² from a broadband source 220 nm to 260 nm; post exposure bake (PEB) at 100 °C for various times. Figure 5a shows the fluorescence yield (bulk) spectrum from the samples. A strong carbonyl peak is present in the PAB, and PAB / UV treated samples, which overlap each other. After a 20 s PEB at 100 °C, the peak at 290.3 eV decreases, but not completely. Even after 2 min PEB, the peak at 290.3 eV is not completely gone.

Figure 5b shows the electron yield (surface) spectra for the same PBOCSt / PFOS films. After both the PAB and a PAB + UV, the C=O π^* transition at 290.3 eV is large in the electron yield (Figure 5b) indicating the polymer is still protected. However, after a short 20 s PEB at 100 °C, the carbonyl peak completely disappears in the electron yield indicating complete deprotection at the film surface. Also shown in Figure 5b is the curve for the PBOCSt / PFOS film after 2 min PEB, and a PHS / PFOS film after a PAB. These curves overlap with the PBOCSt / PFOS film after the 20 s PEB in the carbonyl region near 290.3 eV, verifying that complete surface deprotection occurs in the first 20 s of post exposure baking. Comparison of the electron yield with the fluorescence yield spectrum clearly illustrates that the surface reaction rate is faster than the bulk. In addition, the electron yield spectra exhibit strong

carbon-fluorine peaks between (292 and 298) eV from the PFOS. Since these peaks are not observed in the fluorescence yield spectra this illustrates significant PFOS segregation to the film surface. This large surface segregation of the PAG would lead to a higher acid content near the air interface and increase the deprotection reaction rate. The PFOS is present in small quantities in the bulk of the film (0.05 mass fraction of PFOS relative to polymer, 0.013 mole fraction of PFOS relative to PBOCSt monomers). At small PFOS concentration, the large carbon background from the PBOCSt polymer will dampen the contribution of the C-F peaks from PFOS. Since the C-F peaks are easily observable in the electron yield but not in the fluorescence yield, this qualitatively verifies a strong surface enrichment of the PFOS (as was illustrated in Figure 4).

In Figure 5, there were no delay times between successive processing steps: spin coat, PAB, UV exposure, PEB. However, time delays between the various steps can have a significant impact on the resultant lithographic patterns. Figure 6 shows the carbon K-edge fluorescence (Figure 6a) and electron yield (Figure 6b) spectra for a PBOCSt / PFOS film after the PAB only, and after a PAB + UV + PEB sequence. The NEXAFS spectra in Figure 6a,b are from the same sample. However, for this sample a (5 to 10) min delay time was incorporated between the UV exposure and PEB; this is called a post exposure delay (PED). In the carbon edge fluorescence yield spectra, a carbonyl peak at 290.3 eV is observed in the PAB film. After UV exposure and a 2 min PEB at 100 °C, the peak area has dramatically decreased, indicating deprotection in the bulk of the resist film (Figure 6a). In the carbon edge electron yield spectra, the peak decreases only slightly after UV exposure and PEB, indicating incomplete deprotection at the film surface (Figure 6b).

The mechanisms leading to the incomplete surface deprotection reaction due to PED have not been determined and are a focus of our current research. One possible explanation is acid neutralization in the resist film due to atmospheric contaminants. Nalamasu et al. showed that the PED time was critical to the performance of chemically amplified resists⁸. A PED of several minutes led to an aqueous-base insoluble residue at the resist / air interface, while longer PEDs prevent the lithographic image from being developed⁸. It was shown that resist performance deteriorated dramatically in basic environments, but could be improved by controlling the processing atmosphere or coating the resist with a base-neutralizing (weakly acidic) polymer layer⁸. Incomplete deprotection near the resist / air interface was suggested as the cause of the insoluble residual layer⁸. MacDonald et al. also showed that airborne amine contaminants degrade resist performance by leading to the formulation of a thin insoluble skin at the resist / air interface¹¹. Hinsberg et al. illustrated that the extent of base contamination in a resist film depends on the polymer solubility parameter, and the temperature difference between the PAB and the polymer glass transition¹². The extent of resist contamination will depend on the polymer-contaminant interaction as well as the physical and thermal properties of the resist films.

PED is considered to be a critical factor in t-topping^{8,31}. These experiments illustrate that a PED between (5 and 10) min can lead to incomplete surface deprotection, explaining the insoluble skin in t-topped or closed resist patterns with PED incorporated in the processing. The PAB temperature of 100 °C for these PBOCSt / PFOS films was below the glass transition of bulk PBOCSt ($T_g \approx 130$ °C). By comparison to the work of Hinsberg et al.¹² this would lead to an uptake of atmospheric contaminants by the resist film, since more contaminant absorbs in resists with PAB temperatures well below the bulk polymer T_g . In addition, the incomplete surface deprotection was observed in these PBOCSt / PFOS films despite having significant excess PFOS at the film surface. Apparently atmospheric contamination can still neutralize the excess surface acidity. Qualitatively we observed that short PED (< 15 min) led to surface quenching of the deprotection, while the bulk reaction still proceeded. For longer PED times (> 15 min) both the surface and bulk reaction was quenched as no significant decrease in the carbonyl peak in either the electron or fluorescence yield spectra were observed for these longer times. This is consistent with a process involving contaminant absorption on the film surface and gradual diffusion of the contaminant into the bulk of the film.

3.2 Surface Depth Profiling with NEXAFS

The electron yield signal is surface sensitive. By adjusting a negative voltage bias on the electron yield detector, different effective surface sampling depths can be probed. Figure 7 shows a schematic of the process. When the polymer film is excited by the incident X-ray radiation, the entire region of the film that absorbs photons also emits electrons. The electrons emitted deep within the film cannot escape. Only the electrons emitted near the top (1 to 10) nm from the film surface have enough energy to escape the surface potential. The electron yield detector has a grid where a negative voltage bias can be placed across the grid. The electrons that escape the surface of the film, but were emitted from furthest within the film will be low in energy due to inelastic interactions with

other atoms. These low energy electrons will not have enough kinetic energy to pass the negative detector bias. If the negative detector bias is gradually increased, progressively higher energy electrons are detected, and the effective electron yield sampling depth is closer to the film surface.

We take advantage of this surface depth profiling capability in order to study the chemical composition profile of a model developed line edge region. Bilayer samples were made as described in the experimental section and elsewhere^{27,28}. Briefly, a layer of PBOCSt was spun on a silicon wafer. A second layer of PHS was spun on top of the PBOCSt. The PHS layer was also loaded with the PAG, PFOS. The samples were exposed to UV radiation, post exposure baked (PEB) for various temperatures and times. During the PEB, the acid diffuses into the PBOCSt underlayer, and initiates a diffusion / deprotection front that propagates into the underlayer. Finally, the films were developed in 0.26 N tetra-methyl-ammonium-hydroxide (TMAH) solution, which rinses away the top soluble portion of the film. We suspect that the breadth of the diffusion / reaction front in the line edge region will impact the development process and corresponding LER. Therefore it is important to develop techniques to measure the composition profile of the line edge region. We start by utilizing NEXAFS surface depth profiling on the model bilayer interfacial regions.

Figure 8 shows NEXAFS pre- and post-edge jump normalized spectra in the carbonyl absorption region, between (288 and 292) eV, for the bilayer samples after various PEB times at 90 °C and development in TMAH solution. For these NEXAFS spectra, the detector bias was fixed at -200 eV (sampling depth of roughly 3 nm, or three monomeric layers). Since the electron density of both PHS and PBOCSt are similar, fixing the detector bias essentially fixes the surface sampling volume. The top spectra is for the PBOCSt / PHS bilayer without a PEB and after development in TMAH. In this sample, no deprotection occurs in the PBOCSt underlayer, and the carbonyl absorption is large. However, the carbonyl absorption clearly decreases with increasing bake times, indicating that the extent of deprotection in the surface sampling volume is increasing. The surface composition of the developed bilayer is changing with increasing PEB times. One possible explanation is that the decrease in the surface deprotection is due to broadening of the diffusion / reaction profile at short times leading to a broader surface composition profile in the developed bilayer. Schematic A in Figure 8 illustrates qualitatively this broadening profile through the effective measurement volume as a function of bake time. Another possible explanation is that the actual PBOCSt composition at the film surface is decreasing with increasing bake times, illustrated by Schematic B in Figure 8.

Figure 9 shows the NEXAFS spectra as a function of detector bias for a bilayer sample that was subjected to a short 15 s PEB at 90 °C. The spectra are both pre- and post-edge jump normalized so the carbonyl peak area represents the carbonyl group fraction in the sampling volume. As the negative detector bias increases, the effective electron yield sampling depth is progressively closer to the film surface (as shown by the dotted lines in the schematic in Figure 7). The carbonyl peak area for this short PEB sample does not change dramatically with detector bias. This means that the composition does not change with the changing surface depth sampling volume, and indicates a diffuse surface composition profile over the total sampling volumes scanned with the various detector bias settings (see schematic in Figure 7).

Figure 10 shows the NEXAFS spectra as a function of detector bias for a bilayer sample that was subjected to a 60 s PEB at 90 °C. Again the spectra are both pre- and post-edge jump normalized. However, the carbonyl peak area decreases with increasing detector bias. Again, since the sampling area in the electron yield is progressively closer to the film surface with increasing detector bias, a decrease in the carbonyl peak area with increasing bias indicates a change in the surface composition and a composition change over the sampling volumes scanned with the differing bias settings (see schematic in Figure 10). A comparison of the bias dependence of the carbonyl peak areas at 15 s (Figure 7) and 60 s (Figure 8) PEB times, illustrates a dramatic change in the surface composition profile after development with increasing bake times. Qualitative comparison of the carbonyl peak area (288 to 292) eV shows that for the short PEB (15 s at 90 °C) the peak areas are larger than for the longer PEB time (60 s at 90 °C). This illustrates that the surface PBOCSt fraction is larger for the short bake times and suggest that Schematic B in Figure 7 is the more appropriate representation of the surface composition profile changes with increasing bake times. While the surface composition profile changes with time, it is unclear how the breadth of the buried reaction / diffusion profile (before development) influences the corresponding dissolution process and the resulting surface composition profile and line edge roughness. While these areas are currently under investigation by a number of research groups, the development of high-resolution measurement capabilities allows the potential to make these connections. We are currently developing a theoretical formalism to quantitatively extract the surface composition profile from the NEXAFS bias dependant spectra.

4. CONCLUSIONS

Exploiting the chemical and surface sensitivity of NEXAFS proved useful for probing critical interfacial problems facing sub-100 nm patterning by photolithography. First, segregation of a photoacid generator was observed at the resist/air interface. This surface segregation led to a higher acid content and faster deprotection reaction at the interface relative to the bulk of the film. NEXAFS also proved that a post exposure delay slowed the deprotection reaction at the resist/air interface, presumably due to absorption of atmospheric contaminants on the film surface. Second, a NEXAFS surface depth profiling technique was developed and applied to a model resist line edge region. The depth profiling illustrated that the surface composition of a line edge region is not constant at the assumed solubility switch of the resist, but dependent on the PEB temperature and time. The depth profiling technique has potential to extract surface compositional gradients from patterned surfaces.

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22. Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or

endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment are necessarily the best available for the purpose.

23. For detailed information about the NIST/Dow Soft X-ray Materials Characterization Facility at NSLS BNL, see: <http://nslsweb.nsls.bnl.gov/nsls/pubs/newsletters/96-nov.pdf>
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7. FIGURES

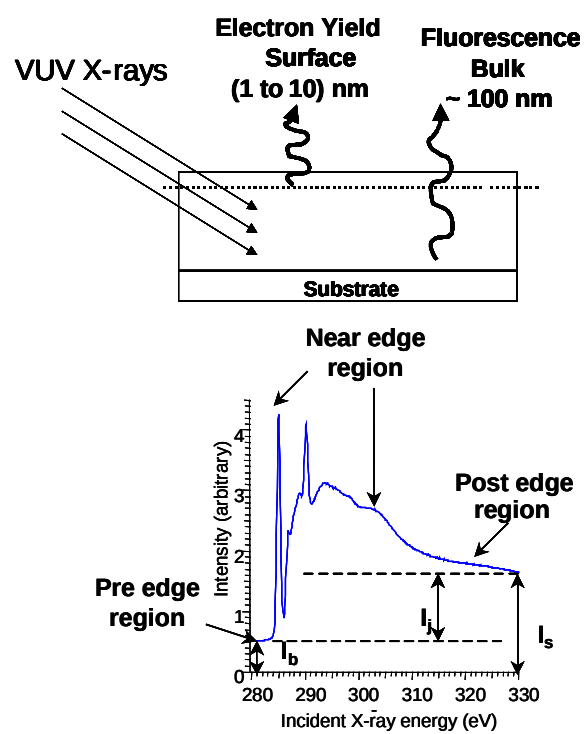


Figure 1. A schematic is shown of the NEXAFS experiment and typical spectra.

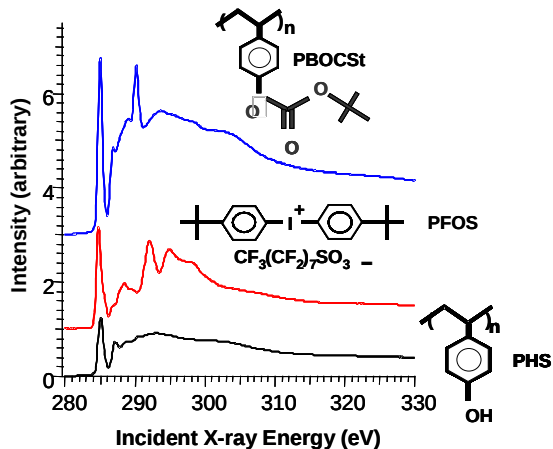


Figure 2. The electron yield NEXAFS spectra are shown for the pure resist components. The top spectra is for PBOCSt. The middle is for PFOS. The bottom is for PHS.

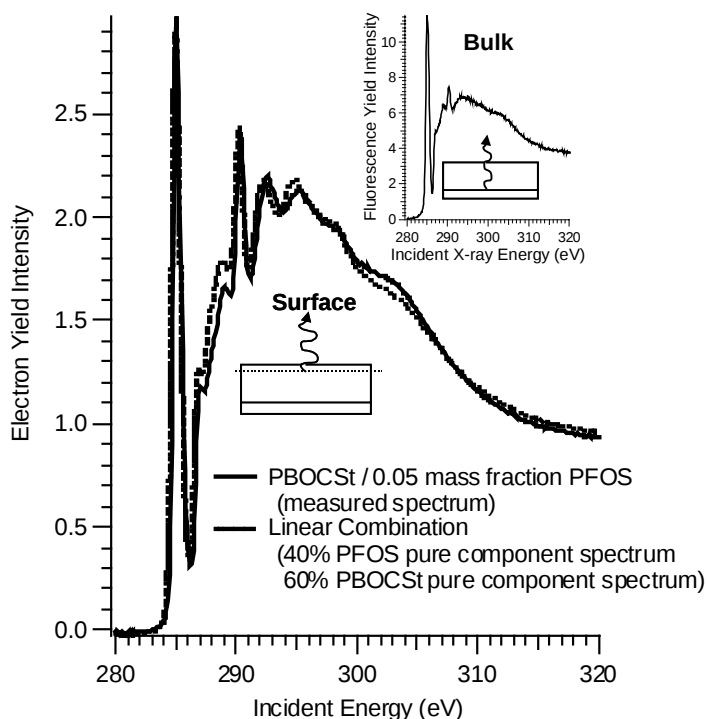


Figure 3. An appropriate linear combination of the pure component electron yield (surface) spectra from PFOS and PBOCSt (dotted line) is used to match the measured electron yield spectrum for PBOCSt / PFOS films. The inset shows the fluorescence yield (bulk) spectrum for the sample. While the fluorine peaks are strongly observed in the electron yield, they are not present in the fluorescence yield spectrum.

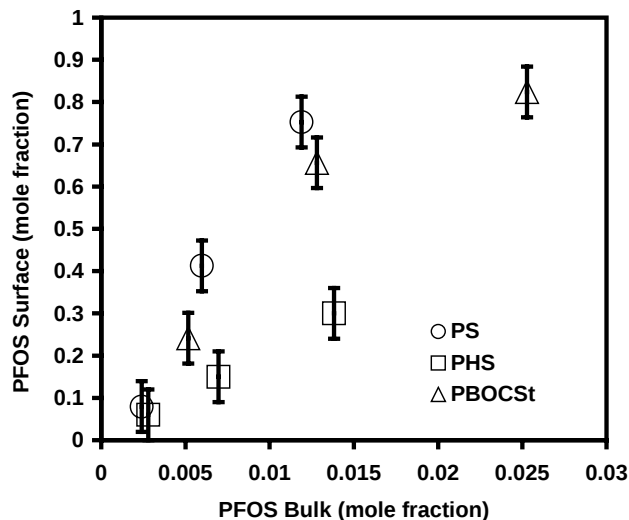


Figure 4. PFOS surface mole fraction (measured by NEXAFS electron yield spectra) plotted against the bulk mole fraction in a variety of polymers.

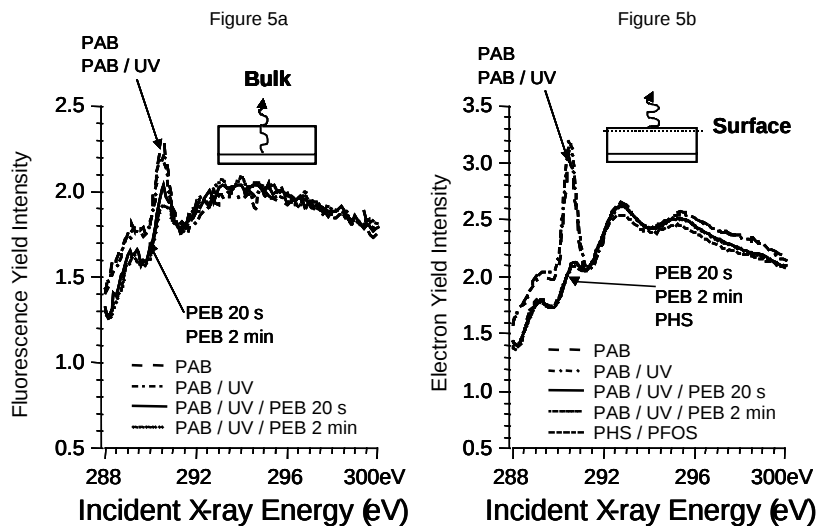


Figure 5. a) The fluorescence yield spectrum (bulk) is shown for the PBOCSt / PFOS films after different processing. b) The electron yield spectrum (surface) is shown for the same PBOCSt / PFOS films. Comparison of the electron and fluorescence yield shows that the surface reaction rate is faster than the bulk.

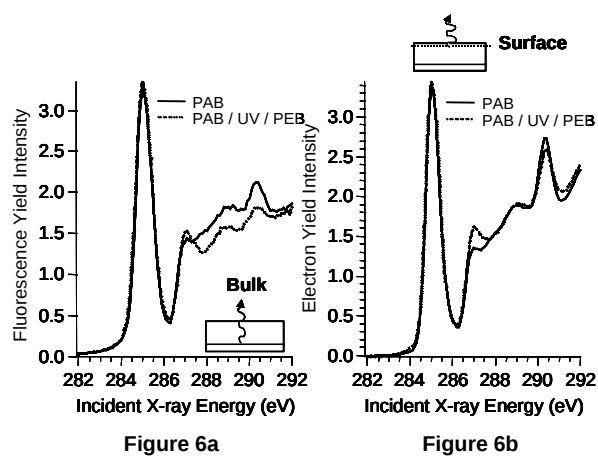


Figure 6. The carbon K-edge fluorescence yield spectra (Figure 6a), and carbon K-edge electron yield spectra (Figure 6b) are shown for the PBOCSt / PFOS film after PAB (solid line) and after UV exposure and a 2 min post exposure bake at 100 °C (dotted line). A post exposure delay of (5 to 10) min was incorporated in the processing.

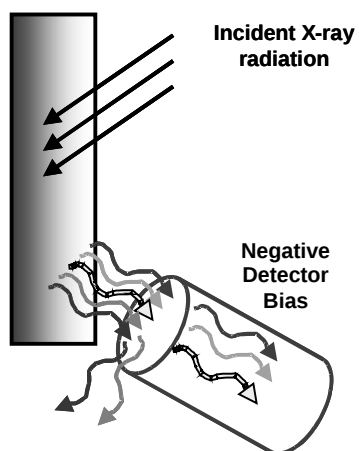


Figure 7. A schematic is shown of NEXAFS surface depth profiling.

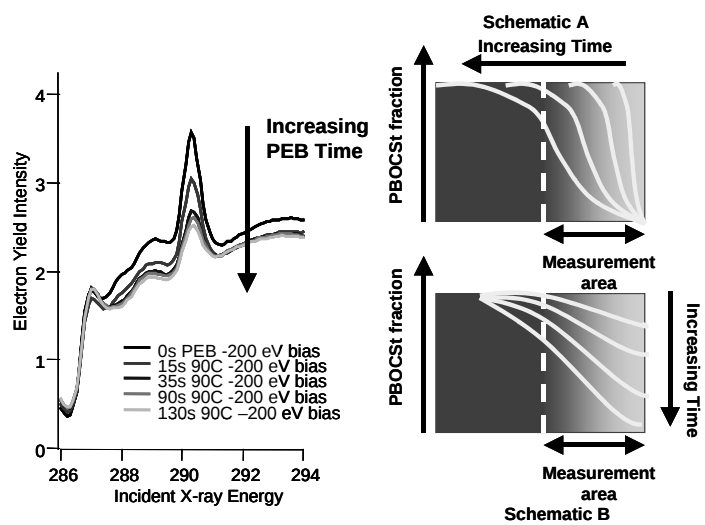


Figure 8. NEXAFS carbon edge electron yield spectra at a constant detector bias of -200 eV are shown for the developed bilayer samples with different PEB times at 90 °C.

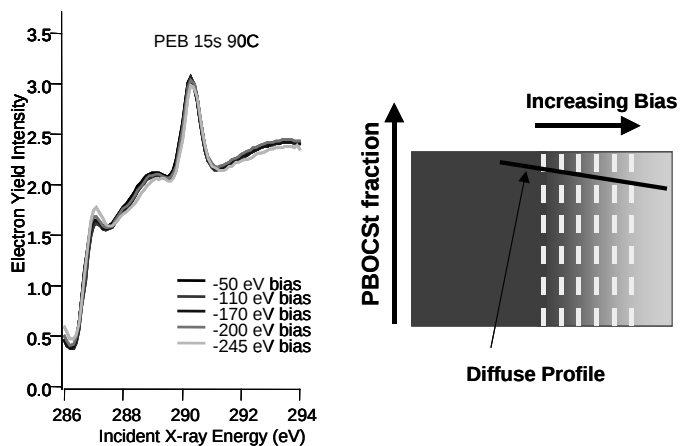


Figure 9. NEXAFS carbon edge electron yield spectra are shown as a function of detector bias for a bilayer with a 15 s PEB at 90 °C. The area of the carbonyl absorption does not change significantly with detector bias.

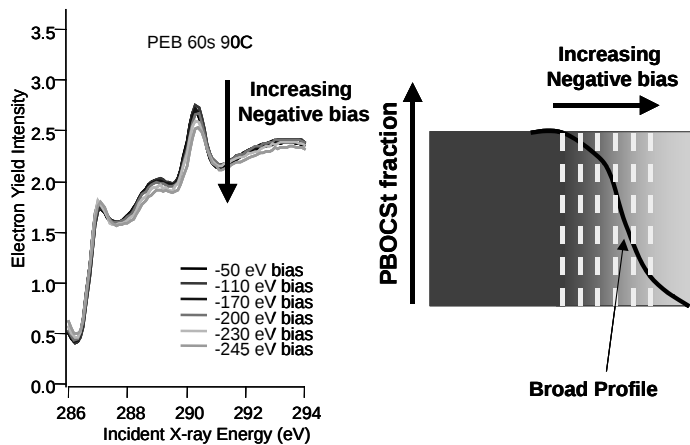


Figure 10. NEXAFS carbon edge electron yield spectra are shown as a function of detector bias for a bilayer with a 60 s PEB at 90 °C. The area of the carbonyl absorption decreases with increasing negative bias.