Probing surface and bulk chemistry in resist films using near edge x-ray absorption fine structure

National Institute of Standards and Technology, 100 Bureau Drive, Stop 8541, Gaithersburg, Maryland 20899-8541

Dario L. Goldfarb and Marie Angelopoulos
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 28 May 2002; accepted 7 October 2002)

The performance of chemically amplified photoresists is extremely sensitive to interfacial and surface phenomena, which cause deviations in the pattern profile near an interface. Striking examples include T-topping or closure near the air/resist interface and footing or undercutting near the resist substrate interface. One focus of our research is to identify mechanisms that cause lithographic patterns to deviate near interfaces. Near edge x-ray absorption fine structure (NEXAFS) is a powerful tool that can be developed and adapted to probe for detailed chemical information near lithographically relevant interfaces. NEXAFS showed that our model resist films exhibited significant surface segregation of the photo acid generator (PAG) at the air interface. The PAG surface mole fraction was 20–70 times greater than the bulk mole fraction and the amount of surface segregation was dependent on the polarity of the polymer. NEXAFS also revealed that the PAG surface fraction was reduced after a postexposure bake. In the absence of delay times between processing steps, the PAG surface enhancement led to a faster deprotection reaction rate near the air interface relative to the bulk. However, when significant postexposure delay times were incorporated into the processing, NEXAFS showed that the surface deprotection reaction was incomplete after postexposure baking. Comparison of carbon K-edge, and oxygen K-edge NEXAFS spectra showed that the incomplete surface reaction was localized at the air interface. While delay effects have previously been linked to deterioration of resist performance, NEXAFS proved to be a valuable tool for providing detailed chemical specificity about the resist surface composition and deprotection kinetics. © 2002 American Vacuum Society. [DOI: 10.1116/1.1524970]

I. 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 polymers. 1 Many factors can impact both CD and LER, including segregation of the photo-acid generator molecules or resist additives, 2 photogenerated acid diffusion, 3 outgassing of photoresist materials, 4 film thickness effects, 5 and copolymer composition and phase separation between protected and deprotected polymers at the interface between exposed and unexposed areas. 6 Due to the complexity of lithographic processing, many processing parameters such as bake temperature, bake time, exposure dose, etc., must be optimized to control CD. 7

In addition, the performance of chemically amplified photoresists is sensitive to interfacial or surface phenomena, which cause deviations in the pattern profile near the interface. Striking examples include T-topping, closure, footing, and undercutting. Many chemically amplified resists exhibit a dramatic degradation in lithographic performance due to airborne contamination. Resist contaminants and airborne amines were shown to induce a thin base insoluble skin on the resist surface leading to T-topping or closure. 5–12 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. 9,12 Segregation or depletion of resist components such as a photo-acid generator, dissolution inhibitor, or base additives at interfaces is also a potential cause of T-topping. For example, a lower photo-acid generator concentration at the resist/air interface would lead to slower deprotection and possibly incomplete deprotection. Segregation of the dissolution inhibitor to the interface would slow the surface dissolution rate. Photo-acid generator size was shown to influence T-topping behavior supposedly by increasing the hydrophobic character of the resist resulting in an increase in surface inhibition. 13

Due to the complexity of the resist formulations and lithographic processing, it is important to understand the impact of the individual resist components on the deprotection reaction and resulting resist performance. We will demonstrate the utility of near-edge x-ray absorption fine structure (NEXAFS) for providing detailed chemical information about lithographic interfaces, by focusing initially on the T-topping/closure issue and probing the surface and bulk

a) Author to whom correspondence should be addressed; current address: Sandia National Laboratories, P.O. Box 5800, Bldg. 897, Mail Stop 1411, Albuquerque, NM 87185; electronic mail: jllenha@sandia.gov
composition of the photo-acid generator in a model resist formulation. In addition, the extent of deprotection at the resist surface is also studied as a function of the postexposure bake time using NEXAFS.

II. EXPERIMENT
A. Materials and methods

The model resist solution was composed of 0.7 g of protected polymer poly(tertbutyloxycarbonyloxy-styrene, \( M_{n,r} = 15000 \)) (PBOCSt) mixed with 0.035 g [0.05 mass fraction of perfluorooctanesulfonate (PFOS) relative to the polymer] of the photo-acid generator, bis(p-tert-butylphenyl)iodonium PFOS]. This mixture was dissolved in 20 mL of propylene glycol methyl ether acetate. The resist solution was spun cast onto silicon wafers at 1500 rpm for 60 s and then postbaked (PAB) for 60 s at 100 °C. The PBOCSt/PFOS films were blanket exposed to ultraviolet 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 postexposure baked (PEB) at 100 °C for 2 min. Polyhydroxystyrene, \( M_{n,r} = 5000 \), (PHS)/PFOS, and polystyrene, \( M_{n,r} = 24000 \) (PS)/PFOS films were made according to the same procedures described above.

B. NEXAFS

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 \( \approx 0.15 \) eV resolution, was used for all the NEXAFS spectra. The monochromator energy scale was calibrated by the carbon \( K \)-edge \( \pi^* \) transition of graphite at 285.35 eV. All the spectra were recorded at room temperature in the NIST–Dow material characterization chamber¹⁴ at \( 1 \times 10^{-6} \) Pa. The spectra were normalized to the incident beam intensity \( I_b \) 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 proportional counter filled with 200 Torr of P-90 (90% methane, 10% argon) in an energy dispersive mode¹⁵ to reduce background fluorescence from other elements. Surface sensitive partial electron yield measurements were made (probe depth of approximately 3–5 nm) by applying a negative bias on the entrance grid of the channeltron electron detector. For the carbon \( K \)-edge spectra (260–330 eV), the electron yield detector was set with a negative bias of 150 V. For the oxygen \( K \)-edge (510–570 eV) and the fluorine \( K \)-edge spectra (670–740 eV), the negative detector bias was set to 320 and 450 V, respectively. The spectra were collected with the incident beam at the magic angle \( (54.7^\circ) \) relative to the sample in order to remove any polarization dependence. For the NEXAFS spectra in this article the experimental standard uncertainty in the peak position is similar to the grating resolution of \( \pm 0.15 \) eV. The relative uncertainty in the NEXAFS intensity is less than \( \pm 5\% \) and was determined by multiple scans on a sample.

III. RESULTS AND DISCUSSION

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, oxygen, or fluorine \( K \)-edge regions, with energy ranges from 260 to 330, 510–570, or 670–740 eV, respectively. 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 (1–10 nm). The photons are measured from \( \approx 100 \) nm within the sample. Because of the characteristic binding energies, carbon, nitrogen, oxygen, and fluorine core electrons are well separated in energy, giving NEXAFS elemental sensitivity. 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 atom.¹⁶

Figure 1 also shows an electron yield NEXAFS spectrum for PBOCSt. The incident x-ray radiation is scanned over the energy range of interest, which is the carbon \( K \) edge between 260 and 330 eV. 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 \( I_s \) is defined as \( I_s = I_b \). In the postedge region the signal intensity \( I_s \) represents the 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 article are pre-edge jump normalized to zero, by subtracting $I_b$ from the spectrum.

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 $\pi^*$ 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 $\pi^*$ transition of the carbonyl on PBOCSt. The middle spectrum, for the PFOS photo-acid generator, also displays a sharp carbon–carbon $\pi^*$ transition similar to PBOCSt. However, the broad peaks between 292.0 and 298.0 eV are due to $\sigma^*$ 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 $\pi^*$ 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 direct monitoring of the deprotection 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 $\pi^*$ 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 $\sigma^*$ peaks (at 292.0 and 298.0 eV) from the PFOS are clearly visible as well as the $\pi^*$ transition associated with the carbonyl on PBOCSt (290.3 eV) and carbon–carbon double bonds on the ring (285.0 eV). Using the pure component electron yield spectra from Fig. 2, the measured electron yield spectra for the PBOCSt/PFOS film (solid line) in Fig. 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 $\sigma^*$ 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 Fig. 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 Fig. 1 in arbitrary units) for PBOCSt was 1.17 and for PFOS was 0.41. The linear combination in Fig. 3 gives 0.4/0.6 as the ratio of carbon signal from PFOS relative to the 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 = $(1.9 + 1)$. The primary uncertainty associated with measuring the PFOS surface mole fraction was 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.

Table I shows the PFOS surface mole fraction estimated from the linear combination of the pure component spectra. 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 nonpolar PBOCSt, and PS polymers. With PS and PBOCSt, the surface mole fraction of PFOS is 68 and 50 times the bulk fraction, respectively. With PHS the surface mole fraction is approximately 20 times the bulk value. The inset in Fig. 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.

The polymer/PFOS films exhibit significant surface PFOS enrichment after PAB. However, it is possible that the surface PFOS composition changes during resist processing. Figure 4 shows the fluorescence yield spectrum (from the bulk of the film) and the electron yield spectrum (from the film surface) at the fluorine edge for a PBOCSt/PFOS film. The signal intensity in the fluorine edge region is due to the fluorine bonds in the PFOS photo-acid generator. The polymers used in this study do not contain fluorine and the neat polymer NEXAFS signal in the fluorine edge region is zero. The fluorine signal in the fluorescence yield (bulk) remains constant after a PAB, PAB + ultraviolet (UV) exposure, and a PAB + UV exposure + PEB, illustrating that the PFOS is not significantly lost from the bulk of the film during typical resist processing. However, the fluorine electron yield signal (surface) changes dramatically during identical processing. After UV exposure there is a distinct increase in the surface fluorine content. This increase in the fluorine is likely due to PFOS diffusion from the bulk to the surface after exposure. But, since the sampling volume of the fluorescence yield is much larger compared to that of the electron yield, a corresponding decrease in the fluorescence yield signal is not observed. At this time we do not understand why this surface enrichment occurs. For the PEB treated film, the fluorine signal decreases slightly relative to the signal from the UV exposed film.

This small decrease in the fluorine signal during the PEB indicates a loss of PFOS from the film surface. During PEB, PBOCSt deprotects to form PHS and volatile products (carbon dioxide and butene). As the volatiles leave, the atomic concentration of fluorine in the film will increase. Assuming that the sampling depth of the electron yield does not change significantly during deprotection, which is reasonable since the electron density measured by x-ray reflectivity only changes by roughly 5% due to deporation, the fluorine electron yield signal should increase in proportion to the extent of deporation and the resultant increase in fluorine density. An increase in the fluorescence yield signal due to the increase in fluorine density, however, would not be observed. This is because the fluorescence yield spectra samples the entire film thickness. As the film thickness decreases during deporation, the fluorine density certainly increases. However, the fluorescence yield still probes the entire film thickness and samples the same total number of fluorine atoms. If no PFOS evaporates from the film, then the fluorescence yield intensity will not change due to deporation and film shrinkage.

It becomes further evident that PFOS leaves the film surface when the film shrinkage is accounted for. Complete PBOCSt deporation is accompanied by a 32%–40% decrease in the film thickness, which would also lead to a similar increase in fluorine density and the fluorine electron yield. However, after PEB the fluorine electron yield is similar to the level after the PAB. This translates to a decrease in the PFOS surface concentration of roughly 40% during the PEB.
the surface, since the fluorocarbons will lower the film surface tension and bulk ionic/polar interactions. For example, the fluorine signal increases in PBOCSt after exposure. It is possible caused by a competition between surface energy reduction and bulk mobility even below the bulk glass transition temperature $T_g$ of PHS. Likewise, for polystyrene/PFOS films we observed a constant PFOS surface composition for the sub-$T_g$ PEB, and PFOS depletion during a PEB above $T_g$.

The bulk glass transition temperature $T_g$ of PHS is $\approx 150 ^\circ C$. If the PEB temperature is greater than the glass transition temperature (180 $^\circ C$ for 5 min) then the fluorine electron yield nearly disappears. However, no change in the electron yield was observed (relative to the UV exposed film) when the PEB is below the glass transition (120 $^\circ C$ for 5 min). It is difficult to decipher whether the PFOS is evaporating from the film surface, or diffusing into the bulk of the film. However, as mentioned previously, the constant fluorescence signal indicates no large-scale evaporation of the PFOS. It is interesting that the electron yield signal only changes during a PEB above the $T_g$ of PHS. Likewise, for polystyrene/PFOS films we observed a constant PFOS surface composition for the sub-$T_g$ PEB, and PFOS depletion during a PEB above $T_g$.

Figure 4 shows that the PFOS surface composition decreased during PEB at 100 $^\circ C$ for PBOCSt films, well below the bulk glass transition temperature for PBOCSt of $\approx 130 ^\circ C$. Since for PS and PHS films, the surface PFOS fraction only changed for bakes above the bulk polymer $T_g$, this suggests that the PBOCSt/PFOS films have significant mobility even below the bulk $T_g$ at 100 $^\circ C$, possibly leading to enhanced PFOS diffusivity. This enhanced diffusivity could be due to a reduced glass transition near the air interface (possibly a plasticizing effect from high PFOS surface composition, to residual solvent plasticization, or to free volume changes during the deprotection reaction and the resulting volatilized products). PFOS is known to have a small diffusion coefficient in resist films, so it is somewhat surprising if the PFOS does diffuse from the surface into the bulk of the film. The loss of PFOS from the film surface during baking is possible evidence that the surface composition in the as cast films is not at equilibrium. This could potentially be caused by kinetic entrapment of the PFOS at the surface during the spin casting process. If true, then the high surface PFOS content would lead to a composition gradient and provide the necessary driving force for PFOS diffusion from the surface into the bulk of the film at temperatures above the glass transition.

Figure 5 compares the electron and fluorescence yield for the PBOCSt/PFOS films after various processing conditions. By monitoring the C–O $\pi^*$ transition from the carbonyl on PBOCSt, the extent of deprotection can be followed during processing. In Figs. 6 and 7 the spectra are both pre- and postedge jump normalized. The postedge jump normalization involves dividing the pre-edge jump normalized spectra by the edge jump intensity ($I_j$ from Fig. 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. Figure 6(a) shows the fluorescence yield 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 6(b) shows the electron yield 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 [Fig. 6(b)] 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 Fig. 6(b) is the curve for the PBOCSt/PFOS film after 2 min PEB, and a PHS/PFOS film after a PAB. These curves overlap the PBOCSt/PFOS film after a 20 s PEB in the carbonyl region near 290.3 eV, verifying that complete surface deprotection occurs in the first 20 s of postexposure baking. Comparison of the electron yield with the fluorescence yield spectrum clearly illustrates that the surface reaction rate is faster than the bulk, most likely due to a high acid concentration near the air interface from the PFOS surface segregation. In addition, in the electron yield spectra exhibit strong carbon–fluorine peaks between 292 and 298 eV from the PFOS. These peaks are not observed in the fluorescence yield spectra; corroborating PFOS surface segregation as discussed previously.

In Fig. 6, there were no delay times between successive processing steps: spin coat, PAB, UV exposure, and PEB. However, time delays between the various steps can have a significant impact on the resultant lithographic patterns. Figure 7 shows the carbon K-edge fluorescence [Fig. 7(a)] and electron yield [Fig. 7(b)] spectra as well as the oxygen K-edge electron yield [Fig. 7(c)] spectra for a PBOCSt/PFOS film after the PAB only, and after a PAB+UV+PEB sequence. The NEXAFS spectra in Figs. 7(a)–7(c) are from the same sample. However, for this sample a 5–10 min delay time was incorporated between the UV exposure and PEB. This is called a postexposure 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 decreases slightly after UV exposure and PEB, indicating incomplete deprotection at the film surface [Fig. 7(b)]. In the oxygen K-edge spectra, a peak at 531.5 eV is observed, also due to the π* transition from the carbonyl bond on the protective group. After UV exposure and PEB, the peak decreases significantly but not completely. The carbon K edge emits an Auger electron with energy of 267 eV. The oxygen Auger electron has energy of 513 eV. Since the oxygen Auger electron has more energy than the carbon edge electron, the sampling depth in the oxygen K-edge electron yield spectra is deeper within the film. The carbon electron yield typically has a sampling depth of 1–3 nm. The oxygen electron yield can sample from 1 to 7 nm. Since the carbon edge electron yield shows minimal deprotection, and the oxygen electron yield spectrum shows significant deprotection (not complete deprotection however), this suggest that the incomplete surface reaction is very localized to the film surface. Bulk measurements on the resist film also supported this conclusion. For example, the PBOCSt/PFOS films shrink by 25%–30% after the PEB, consistent with significant resist deprotection. Fourier transform infrared spectroscopy also further verified significant deprotection in the bulk of these films.

The mechanisms leading to the incomplete surface depro-
protection reaction due to PED have not been determined and are the 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 postexposure bake delay time was critical to the performance of chemically amplified resists. A PED of several minutes leads to an aqueous-base insoluble residue at the resist/air interface, while longer PEDs prevent the lithographic image from being developed. 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 layer. Incomplete deprotection near the resist/air interface was suggested as the cause of the insoluble residual layer. 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 interface. 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 postbake temperature and the polymer glass transition. So 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. These experiments illustrate that a PED between 5 and 10 min can lead to incomplete surface deprotection. The PAB temperature of 100 °C for these PBOCSt/PFOS films was below the glass transition of bulk PBOCSt. By comparison to the work of Hinsberg et al. 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 Tg. It is interesting that the incomplete surface deprotection was observed in these PBOCSt/PFOS films, where despite having significant excess PFOS at the film surface, atmospheric contamination can still neutralize the excess surface acidity.

**IV. CONCLUSIONS**

NEXAFS proved a useful tool for probing the surface composition of model resist films. In addition, comparing the fluorescence and electron yield spectra allowed for detecting differences between the bulk and surface composition and deprotection kinetics. The photo-acid generator mole fraction near the air interface was 20–70 times the bulk mole fraction, and depended on the polymer polarity. Larger PFOS surface segregation was observed in nonpolar polymers. The PFOS surface mole fraction decreased during resist processing. For nonprotected polymers such as PHS and PS, the decrease in PFOS surface fraction only occurred during PEB temperatures above the bulk polymer glass transition. The excess PFOS at the film/air interface led to a faster surface deprotection reaction at the interface relative to the bulk. However, when a postexposure delay was incorporated into the processing, the deprotection reaction at the resist/air interface was incomplete after PEB. Atmospheric contamination leading to acid neutralization during the PED is a possible cause of the incomplete deprotection reaction near the air interface. Comparison of the fluorescence yield and electron yield spectra of both the carbon and oxygen edges illustrated that the incomplete surface deprotection was confined to the top surface of the film for these delay times.

**ACKNOWLEDGMENTS**

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. This work was supported by Defense Advanced Research Projects Agency (DARPA) under Grant No. N66001-00-C-8803.