NEXAFS Measurements of the Surface Chemistry of Chemically Amplified Photoresists

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Abstract. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition profile (top 1 nm to 6 nm) of model chemically amplified photoresists with various photo-acid generators. These materials are prone to interfacial and surface chemical changes that cause deviations in the desired lithographic pattern such as T-topping and closure. If interfacial excess or depletion of the photo-generated acid occurs, either from atmospheric contamination, evaporation, or segregation within the film, the resulting compositional heterogeneity will affect the interfacial photoresist structure, composition, and deprotection kinetics. A significant technical challenge lies in measuring the surface composition and extent of reaction with depth resolution at interfaces. Electron yield NEXAFS allows measurement of the surface chemical composition, particularly for carbon, fluorine, oxygen, and nitrogen. When exposed to vacuum ultraviolet x-rays (soft x-rays), the top surface of the material releases electrons that can be measured with a high pass grid analyzer electron yield detector. By varying the negative voltage bias at the entrance grid to the electron yield detector, it is possible to differentiate the kinetic energy of electrons escaping from depths up to 6 nm into the film. This measurement capability becomes increasingly important with the drive towards sub-100 nm lithography. As the photoresist film thickness continually decreases and the interfacial regions dominate the behavior of the material, it is crucial to understand both their physical and chemical nature.

INTRODUCTION

With the drive toward sub-100 nm lithography and the subsequent need for changing photoresist platforms, techniques that are able to access surface versus depth information in such materials become instrumental in determining failure mechanisms, chemical changes, distribution of components, etc. For example, in chemically amplified photoresists it is possible for small molecule additives such as the photo-acid generator (PAG) to segregate to the surface of the photoresist. During application of the photoresist formulation to the wafer, post application bake (PAB), and post exposure bake (PEB), the surface of the photoresist may become enriched in PAG, affecting the resulting deprotection kinetics and/or dissolution behavior during development, particularly for PAGs that can also act as dissolution inhibitors. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy is especially useful in the investigation of surface chemistry of photoresists.

In general, NEXAFS can probe both the surface (up to 6 nm) and bulk (up to 200 nm) chemistry, and it is possible to observe changes in the surface region as compared to the bulk of the film. Previously, NEXAFS has been used to quantify the segregation of PAG to the photoresist surface for model systems[1]. In this paper, we report the NEXAFS carbon *K*-edge electron yield (surface) spectra of model chemically amplified positive tone photoresists and their interactions with different PAGs. It has also been shown that post exposure delay (PED) can introduce dissolution problems at the surface of the photoresist[2]. We have explored the effect of introducing PED into the photoresist processing to observe changes in the deprotection chemistry. With the ability to depth profile up to 6 nm into the film surface, it is possible to observe the effects of PAG segregation and PED within this small sampling depth.
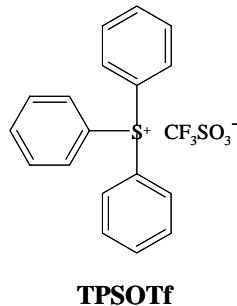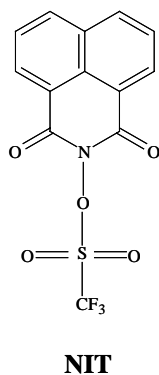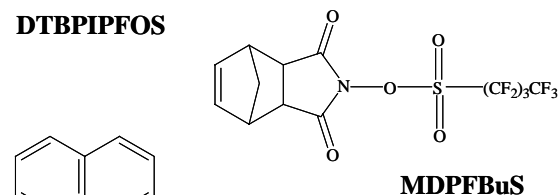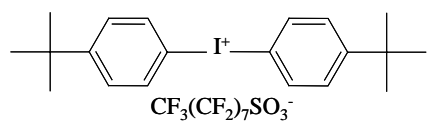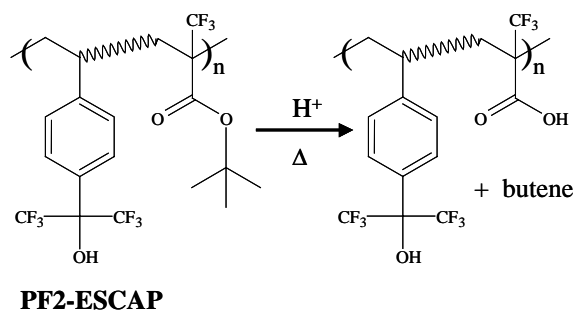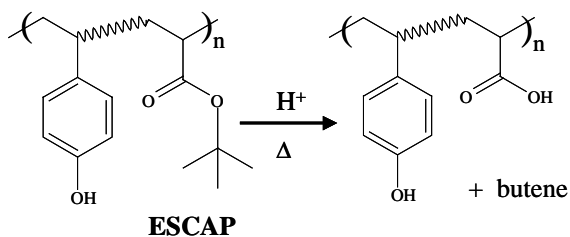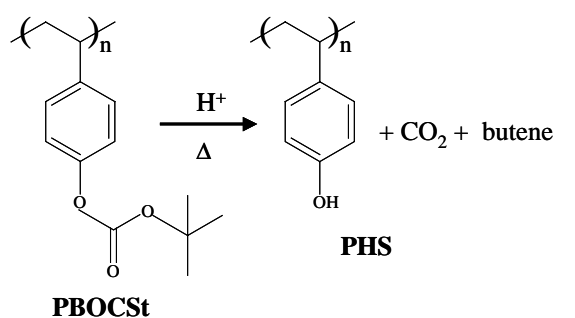
FIGURE 1. Chemical structures of model photoresists and PAGs used in this study.

EXPERIMENT

Materials and Methods

Four model photoresists were used in this study: poly((*t*-butoxycarbonyloxy)styrene) (PBOCSt), poly(4-hydroxystyrene) (PHS), poly(4-hydroxy-styrene-co-*t*-butyl acrylate) (ESCAP), and poly(*t*-butyl trifluoromethacrylate-co-styrene hexafluoro-alcohol) (P(TBTFMA-STHFA)), referred to as PF2-ESCAP. The PAGs used were di(4-*t*-butylphenyl) iodonium perfluorooctanesulfonate (DTBPIPFOS), triphenylsulfonium trifluoromethanesulfonate (TPSOTf), N-trifluoromethanesulfonyloxynaphthal-imide (NIT), and N-hydroxy-5-norbornene-2,3-dicar-boximide perfluoro-1-butanesulfonate (MDPFBuS). The structures and deprotection reactions of the resists are shown in Figure 1. Samples were prepared by solvent casting various formulations of photoresist and PAG onto a silicon wafer, followed by PAB, UV exposure, and PEB. Some samples were subject to PAB only. Samples for which a PED is reported were held for that time in atmosphere after UV exposure, before PEB.

NEXAFS Spectroscopy

NEXAFS measurements were conducted at the U7A beam line of the National Synchrotron Light Source at Brookhaven National Laboratory. The experimental conditions have been described elsewhere[1]. The spectra were collected with the incident beam at the magic angle (54.7°) relative to the sample to remove any polarization dependence. For the NEXAFS spectra in this paper the experimental standard uncertainty in the peak position is $\approx \pm 0.15$ eV. The relative uncertainty in the NEXAFS intensity is less than ± 5 % and was determined by multiple scans on a sample.

In a typical NEXAFS experiment, soft 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. Due to the well-defined energy gap associated with a core shell to unoccupied orbital transition, NEXAFS is sensitive to the bonding characteristics of the atom giving a discrete peak for each chemical bonding environment. Auger electrons are emitted when the excited core electron from the irradiated sample relaxes. The electrons emitted deep within the film cannot escape; only the electrons emitted near the top (1 nm to 6 nm for carbon *K*-edge electron yield spectra) of the film surface have enough kinetic energy to escape the surface potential. The electron

yield detector has a grid where a negative voltage bias can be applied. The electrons that escape the surface of the film but are emitted from furthest within the film are low in energy due to inelastic interactions with other atoms. These low energy electrons may not have enough kinetic energy to pass the negative detector bias and are not detected. If the negative detector bias voltage is gradually increased, progressively higher kinetic energy electrons are detected, and the effective electron yield sampling depth gets closer to the film surface.

RESULTS AND DISCUSSION

The NEXAFS carbon K-edge electron yield (surface) spectra of neat PBOCSt, PHS, ESCAP, and PF2-ESCAP (PAB only) at variable bias voltages are shown in Figures 2(a)-(d), respectively. The spectra are pre- and post-edge normalized[1] to remove spectral dependence on total carbon content; therefore, differences in the spectra are indicative of changes in chemistry. In each of the figures, all spectra taken at different bias voltages (−50 V, −100 V, −150V, and −200 V) overlay identically, indicating that there are no significant changes in the surface chemistry of these neat photoresists up to ≈ 6 nm. For each of the spectra, the first peak at 285.0 eV corresponds to the C 1s $\rightarrow \pi^*_{C=C}$ transition from the styrene ring. A splitting of the $\pi^*_{C=C}$ resonance in PHS is visible at ≈ 287.5 eV [3]. For PBOCSt, the carbonyl C 1s $\rightarrow \pi^*_{C=O}$ transition is reflected in the peak at 290.3 eV; this peak is absent from the PHS spectra. Because of the loss of CO_2 (resulting in diminished $\pi^*_{C=O}$ peak) during deprotection of PBOCSt to form PHS, it is possible to follow the extent of this reaction using NEXAFS [1]. In ESCAP and PF2-ESCAP, the carbonyl C 1s $\rightarrow \pi^*_{C=O}$ transition occurs at 288.5 eV. Neither ESCAP nor PF2-ESCAP has a loss of carbonyl during deprotection, therefore it is necessary to compare the relative changes in $\pi^*_{C=C}$ and $\pi^*_{C=O}$ peak heights to determine deprotection, as shown below in Table I and Figures 3 and 5. The broad peaks between 292.0 eV and 298.0 eV correspond to C 1s $\rightarrow \sigma^*$ transitions. The spectra for PF2-ESCAP, in Figure 2(d), are noticeably different from the others in Figure 2 in the area of 293 eV to 298 eV. The large peak at 295.0 eV and smaller peak at 297.5 eV correspond to the C-F σ^* transitions (see Figure 1).

Table I provides an approximate ratio of particular bonds to total carbon content in the protected and deprotected photoresists. For ESCAP and PF2-ESCAP, comparison of these ratios is needed to determine extent of deprotection.
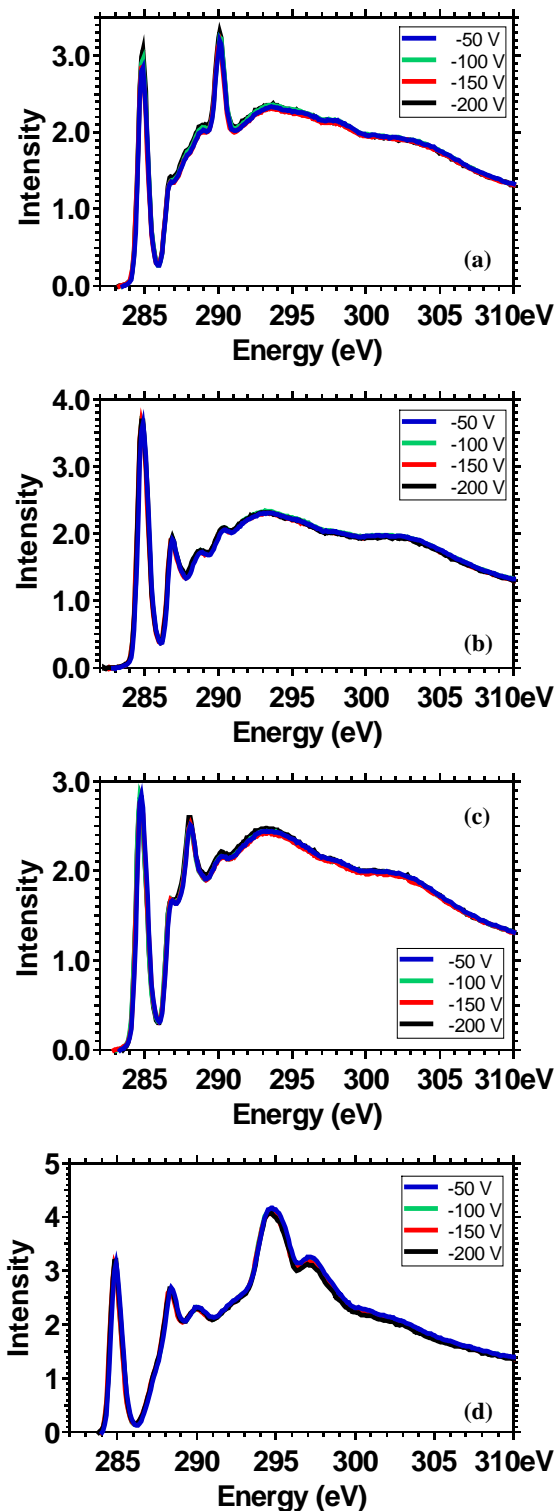

FIGURE 2. NEXAFS carbon K-edge electron yield (surface) spectra at variable detector bias.
(a) PBOCSt, (b) PHS, (c) ESCAP, (d) PF2-ESCAP.

TABLE I. Approximate bond:carbon ratio for selected bonds in protected v. deprotected photoresists (based on number of carbon atoms in model repeat unit) for comparison of relative peak height in NEXAFS spectra.

Photoresist	Bond	Protected	Deprotected
PBOCSt	C=C	6/14	6/9
	C-H	18/14	9/9
	C=O	1/14	0
ESCAP	C=C	6/15	6/11
	C-H	19/15	10/11
	C=O	1/15	1/11
PF2-ESCAP	C=C	6/18	6/14
	C-H	18/18	9/14
	C=O	1/18	1/14

Figures 3(a) and 3(b) are a comparison of neat ESCAP and ESCAP with 4 % mass fraction of DTBPIPFOS at –50 V bias ($\approx$ 6 nm) and –250 V bias ($\approx$ 1 nm), respectively. All samples (including the neat material) in these spectra were processed with PAB at 130 °C for 60 s, UV exposure of 120 mJ/cm^2 from a broadband source with wavelengths from 220 nm to 260 nm, PED from 0 s to 600 s, and PEB at 100 °C for 60 s. The spectra differ significantly in the area of 292 eV and 295 eV due to the C-F σ^* peaks corresponding to DTBPIPFOS, indicative of segregation of this component to the photoresist surface.

In comparing neat ESCAP to ESCAP processed with no PED (i.e., deprotected ESCAP) in Figure 3(a), the $\pi^*_{C=C}$ peak has clearly increased in the deprotected ESCAP spectrum. For the spectra of the samples processed with PED, however, there is almost no change in the $\pi^*_{C=C}$ peak, indicating a lack of deprotection (no loss of butene). The sample is not stable with PED; the spectrum of the sample with a 60 s PED differs from that with 600 s PED. In Figure 3(b), all spectra of the processed ESCAP overlay, taken at –250 V bias (top 1 nm of the material). This is typical of spectra for all photoresists in the study at –250 V bias, indicating that the very surface of the material is always subject to comparable chemical changes to those seen further into the surface of the films processed with PED. This trend indicates that the surface of the film is always susceptible to these chemical changes and that during PED, the material further into the surface undergoes the same chemical changes, leading to failure of the materials. Also, the $\pi^*_{C=C}$ and $\pi^*_{C=O}$ peaks are of lower intensity in the PED spectra. The lower intensity peaks can be attributed to the post-edge normalization, which removes spectral dependence on total carbon content; because the

surface has high fluorine content, the carbon density is reduced, leading to the lower intensity of the $\pi^*_{C=C}$ and $\pi^*_{C=O}$ peaks because of the segregation of the fluorinated PAG to the photoresist surface.
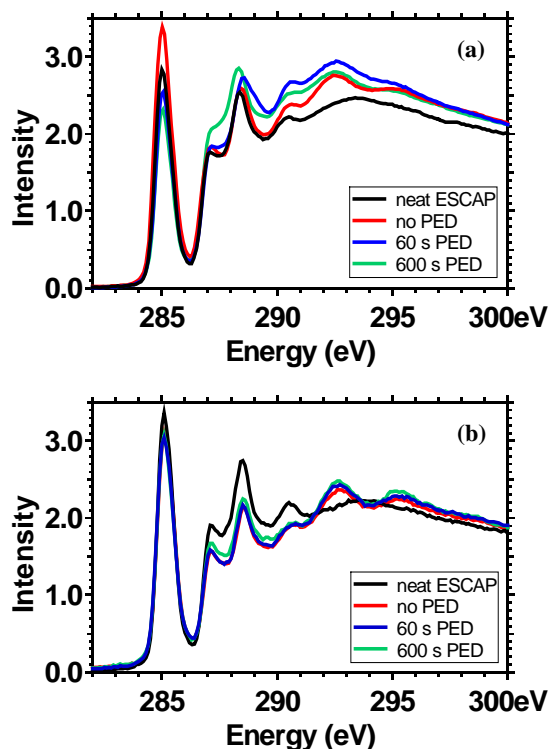

FIGURE 3. NEXAFS carbon K-edge electron yield (surface) spectra of ESCAP with DTBIOPFOS, variable PED. (a) –50 V detector bias, (b) –250 V detector bias.

Segregation of DTBPIPFOS was reported for formulations of PBOCSt, PHS, and polystyrene with DTBPIPFOS and was found to be a maximum after PAB[1]. As demonstrated here, this segregation of DTBPIPFOS also occurs in ESCAP. The segregation of DTBPIPFOS is not observable in PF2-ESCAP (Figure 5) due to overlap of the C-F peaks corresponding to DTBPIPFOS with the C-F peaks from the photoresist. For the other PAGs no segregation was observed after PAB, as shown in Figures 4(a) and 4(b). Spectra of (a) neat PBOCSt and PBOCSt with TPSOTf, NIT, and MDPFBuS and (b) neat ESCAP and ESCAP with TPSOTf, NIT, and MDPFBuS, (PAB 130 °C for 60 s) at –150 V bias, show no indication of surface segregation of any of these PAGs. DTBPIPFOS is unique in both its ionic character and high fluorine content, leading to a strong tendency to segregate to the photoresist surface. TPSOTf is also ionic, however, its lower fluorine content may make it less segregating.
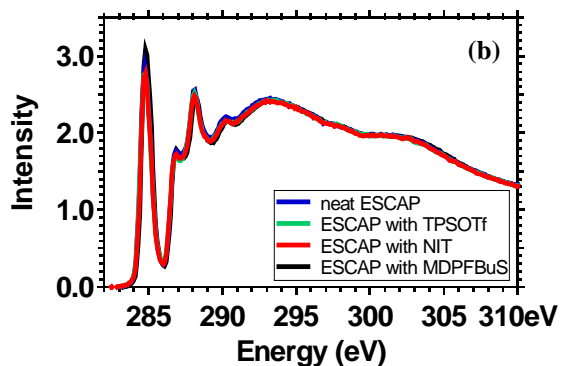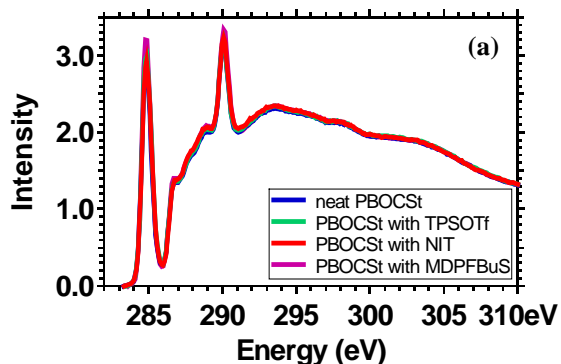
FIGURE 4. NEXAFS carbon *K*-edge electron yield (surface) spectra, taken at −150 V bias, of (a) PBOCSt and (b) ESCAP with various PAGs.

FIGURE 5. NEXAFS carbon *K*-edge electron yield (surface) spectra of PF2-ESCAP with DTBIOPFOS, variable PED. (a) –50 V detector bias, (b) –250 V detector bias.

A comparison of neat PF2-ESCAP and PF2-ESCAP with 3 % by mass of DTBPIPFOS at detector biases of −50 V and −250 V are shown in Figures 5(a) and (b). All samples were processed as above for Figure 3. In Figure 5(a) all spectra of the PF2-ESCAP processed with PED overlay one another. The surface chemistry at 1 nm into the film, as seen in Figure 5(b), is interesting because it implies that there are no differences between the neat material and the formulation. During PED, the chemistry at 6 nm into the film approaches the chemical conditions of the top 1 nm of the surface. This is demonstrated by the change in relative heights of the $\pi^*_{C=C}$ peak and σ^* C-F peak. In Figure 5(a), the σ^* region of the spectra has much higher intensity than the π^* region, but after some PED (stable for times above 60 s) the spectra begin to lose intensity in the σ^* region. The cause of this change in surface chemistry is currently unknown, but investigations are ongoing.

CONCLUSIONS

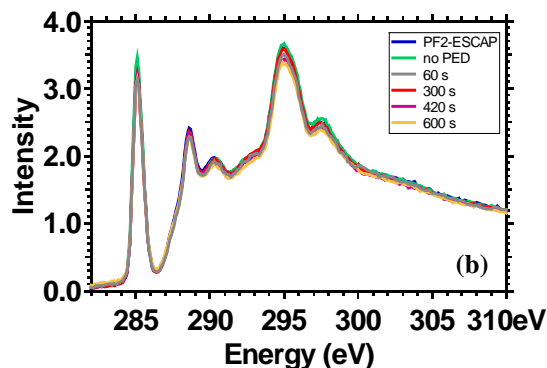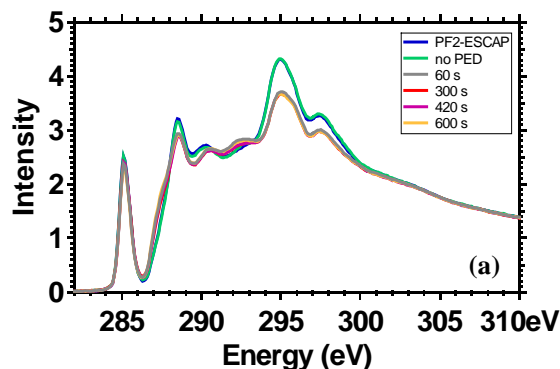NEXAFS is a powerful tool for measuring the depth dependent surface chemistry in model chemically amplified photoresists. The capability to measure both PAG segregation and PED effects on the surface chemistry are important contributions to the understanding of photoresist performance.

ACKNOWLEDGMENTS

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