

# Near edge x-ray absorption fine structure measurements of surface segregation in 157 nm photoresist blends

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The surface and bulk chemistry of photoresist blends for use at the 157 nm node were analyzed using near edge x-ray absorption fine structure spectroscopy to quantify component segregation and identify surface phenomena that may impact pattern formation. Spectral combinations of the constituent polymers are used to fit the spectra of the blend films. Significant segregation of one component to the surface of the photoresist film was found, in excess of the composition of that component in the blend. The bulk data were consistent with initial blend compositions. As expected, the more hydrophobic or lower surface tension component wets the film surface even under typical photoresist processing conditions. © 2003 American Vacuum Society. [DOI: 10.1116/1.1624256]

## I. INTRODUCTION

The microlithography industry continues to require photoresist technology to create patterns for integrated circuitry; however, as desired feature sizes are progressively reduced, physico-chemical problems arise on the length scale of the constituent polymers. In addition, use of the newest generation of thin film photoresists presents a number of materials problems, including polymer/substrate and polymer/air interfacial (surface energy) effects, blend miscibility, small molecule diffusion in thin films, and permeability of airborne contaminants. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy can simultaneously probe the surface and bulk chemistry of these chemically amplified photoresists to determine possible causes of pattern degradation, including polymer component and small molecule diffusion/segregation to the photoresist surface, postexposure delay induced material failure, and interactions between components of the photoresist formulation and developer.

Recently, Ito *et al.* proposed a formulation strategy employing blends of different potential 157 nm fluorinated homopolymers and copolymers.<sup>1</sup> They found that the protected copolymer could beneficially act as a dissolution inhibitor to the homopolymer to provide enhanced patterning capability. However, for polymer blend constituents having different hydrophobicity or surface tension, the more hydrophobic or lower surface tension species will typically wet the blend film surface when heated in air.<sup>2</sup> Preferential wetting of the

blend/substrate interface by one of the blend constituents may also occur.<sup>3</sup> The objective of this study is to characterize polymer component segregation in thin films of 157 nm blend materials by comparing the chemical properties up to 6 nm into the surface with the bulk chemical properties of the film. We find significant segregation of one blend component to the polymer film surface and discuss implications for the performance of thin film blend photoresists.

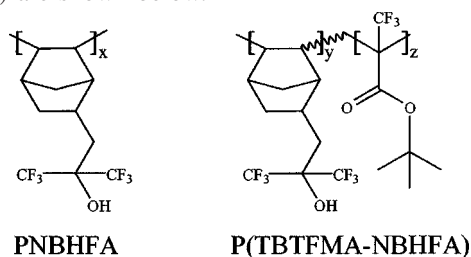
## II. EXPERIMENT

### A. Materials and methods

Two model photoresists were used in this study: poly(norbornene hexafluoroalcohol) (PNBHFA) and poly(*t*-butyltrifluoromethacrylate-co-norbornene hexafluoroalcohol) [P(TBTFMA<sub>0.60</sub>-NBHFA<sub>0.40</sub>)] and the photoacid generator (PAG) di(4-*t*-butylphenyl) iodonium perfluorooctanesulfonate (DTBPIPFOS). Pure component and various blend compositions of PNBHFA and P(TBTFMA-NBHFA) were prepared as 4% mass fraction solutions in propylene glycol methyl ether acetate (PGMEA). Thin films were prepared from these solutions by spin coating onto silicon wafers, followed by a postapply bake at 130 °C for 60 s. Film thickness is on the order of 300 nm. To investigate film thickness effects, one 50:50 (by mass) blend film was prepared from a 2% mass fraction PGMEA solution. In addition, a 50:50 blend film was prepared containing 5% mass fraction DTBPIPFOS from a 4% mass fraction PGMEA solution to investigate possible PAG segregation to the surface of the blend film. The structures of PNBHFA and P(TBTFMA-

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NBHFA) are shown below.



## B. NEXAFS

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.<sup>4</sup> The spectra were collected with the incident beam at the magic angle ( $54.7^\circ$ ) relative to the sample to remove any polarization dependence. For the NEXAFS spectra in this article the experimental standard uncertainty in the peak position is  $\approx \pm 0.15$  eV. The relative uncertainty in the NEXAFS intensity is less than  $\pm 5\%$  and was determined by multiple scans on a sample.

When acquiring NEXAFS spectra, 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 and photons are emitted when the excited core electron from the irradiated sample relaxes. Electrons emitted from deep within the film cannot escape; only the electrons emitted near the top (1–6 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 lack 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.

Photons are emitted from up to  $\approx 200$  nm into the film and are detected by a fluorescence yield detector. In order to obtain adequate bulk spectra, the fluorescence yield is measured for four spots on each sample and the collected spectra are averaged.

## III. RESULTS AND DISCUSSION

NEXAFS carbon *K*-edge spectra of neat PNBHFA and P(TBTFMA-NBHFA) are shown in Fig. 1(i) and (ii), respectively. Electron yield (surface) data at bias voltages of  $-200$  V ( $\approx 3$  nm into the surface),  $-150$  V ( $\approx 4$  nm into the surface), and  $-50$  V ( $\approx 6$  nm into the surface) are desig-

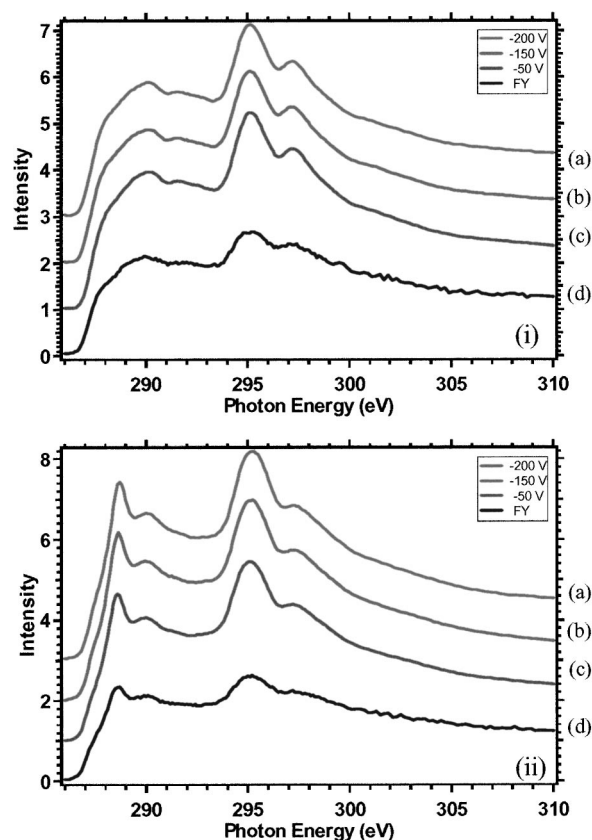


FIG. 1. NEXAFS carbon *K*-edge spectra for neat (i) PNBHFA and (ii) P(TBTFMA-NBHFA). Electron yield (surface) spectra at (a)  $-200$  V; (b)  $-150$  V, and (c)  $-50$  V detector bias; (d) fluorescence yield (bulk) spectra. Spectra are vertically offset for clarity.

nated (a), (b), and (c); fluorescence yield (bulk) data are designated (d). All spectra are pre- and postedge jump normalized. Postedge normalization eliminates the spectral dependence on total carbon content; therefore, changes in the NEXAFS spectra are indicative of changes in chemical functionality. The spectra taken at  $-200$ ,  $-150$ , and  $-50$  V are nearly identical and agree with the fluorescence spectra, indicating there are no depth dependent chemical changes in the neat polymers. The spectra of the neat polymers shown in Fig. 1 will provide the component spectra for the linear combination fits of the blend film spectra.

The spectra shown in Fig. 1(i) and (ii) show a prominent C  $1s \rightarrow \sigma^*_{C-F}$  transition at 295.1 eV. In Fig. 1(ii), the sharp peak at 288.5 eV corresponds to the C  $1s \rightarrow \pi^*_{C=O}$  transition from the carbonyl of TBTFMA and provides a signature peak for this component.

Figure 2 shows the carbon *K*-edge electron yield at different voltage biases and fluorescence yield spectra for three blend compositions (by mass) of PNBHFA with P(TBTFMA-NBHFA); (i) 75:25; (ii) 50:50; and (iii) 25:75.

In Fig. 2, solid lines are the experimental spectra and dashed lines represent a linear combination of the component [PNBHFA and P(TBTFMA-NBHFA)] spectra at the corresponding voltage bias. For example, the  $-50$  V bias spectra of the 50:50 blend film is fit by a combination of 22% PN-

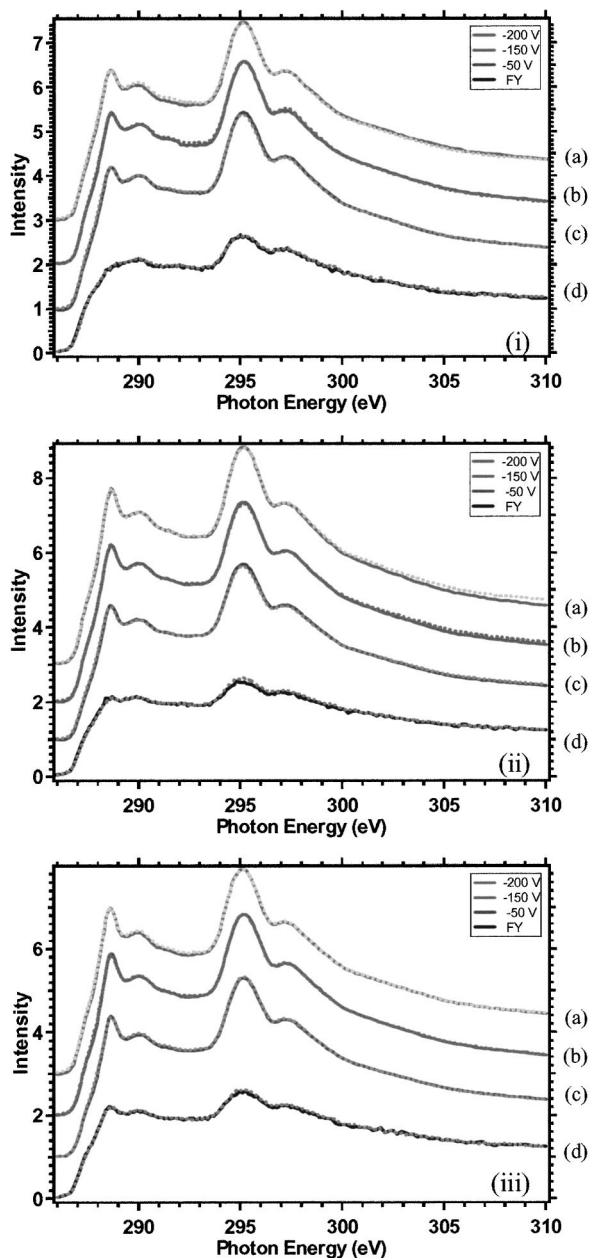


FIG. 2. NEXAFS carbon *K*-edge spectra for (i) 75:25, (ii) 50:50, and (iii) 25:75 mass ratios of PNBHFA with P(TBTFMA-NBHFA). Solid lines are electron yield (surface) spectra at (a)  $-200$  V; (b)  $-150$  V, and (c)  $-50$  V detector bias, and (d) fluorescence yield (bulk) spectra. Dashed lines show fits to the data. Spectra are vertically offset for clarity.

BHFA spectra [Fig. 1(i)] and 78% P(TBTFMA-NBHFA) spectra [Fig. 1(ii)]. For comparison, the bulk spectra is fit by 50% PNBHFA and 50% P(TBTFMA-NBHFA). All of the bulk spectra are fit by linear combinations corresponding to the initial blend compositions. The proportions of component spectra used in the fits are shown in Table I. Unlike the neat polymers, the blends' surface and bulk spectra are significantly different and indicate substantial segregation of the P(TBTFMA-NBHFA) copolymer to the surface of the blend films, evident by the intensity of the C  $1s \rightarrow \pi^*_{C=O}$  peak at 288.5 eV, which is prominent at the surface but much less so in the bulk.

TABLE I. Compositions of the linear combinations of component spectra used to fit the surface spectra of various PNBHFA and P(TBTFMA-NBHFA) blend compositions at  $-150$  V detector bias. Fluorescence yield (bulk) spectra were all fit with constituent spectra in initial blend proportions. \*Corresponds to thin 50:50 blend film,  $\delta$  corresponds to 50:50 blend film with 5% DTBPIFOS by mass. Fits are  $\pm \approx 5\%$ .

Initial blend composition		
PNBHFA:		
P(TBTFMA-NBHFA)	P(TBTFMA-NBHFA)	
75:25		0.62
50:50		0.82
25:75		0.82
50:50*		0.76
50:50 $\delta$		0.78

Figure 3 shows surface copolymer compositions and water contact angles<sup>5</sup> vs bulk copolymer composition. For each blend composition shown in Fig. 3, the composition of copolymer on the blend film surface is greater than the composition in the bulk. In the extreme case, i.e., for the 75:25 blend film, the composition of copolymer at the surface is more than twice that of the bulk (62% vs 25%). It is expected that the copolymer will wet the blend film surface due to its higher hydrophobicity.<sup>5</sup> The contact angle data indicate the same trend. Surface segregation of one blend component after the relatively short bake times typical of photoresist processing is surprising because the glass transition temperatures of these polymers are over  $150^\circ\text{C}$ . However, residual casting solvent present in the blend films could reduce the effective glass transition temperature, facilitating diffusion within the film during the baking process<sup>1</sup> or segregation could occur during spin coating, where the solvent concentration can be significant. Also, we anticipate that the apparent glass transition temperature will depend on film thickness due to the segregation.

The NEXAFS carbon *K*-edge electron yield spectra of a 50:50 blend is shown in Fig. 4 for (i) thinner film (approximately half of the thickness of the films shown above) and (ii) containing 5% DTBPIFOS mass fraction, at (a)  $-200$  V, (b)  $-150$  V, and (c)  $-50$  V biases, and (d) fluorescence yield data. The experimental spectra are shown by the solid curves; fits are shown by dashed curves. The spectra in Fig. 4(i) were fit with 24% PNBHFA surface compo-

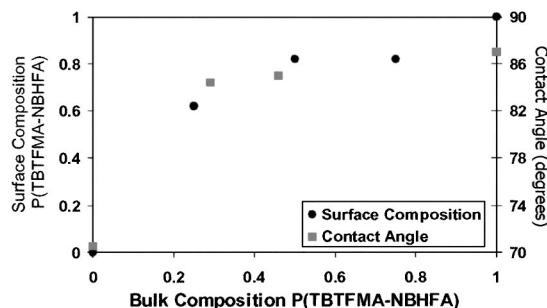


FIG. 3. Surface copolymer composition and contact angle as a function of initial blend composition.



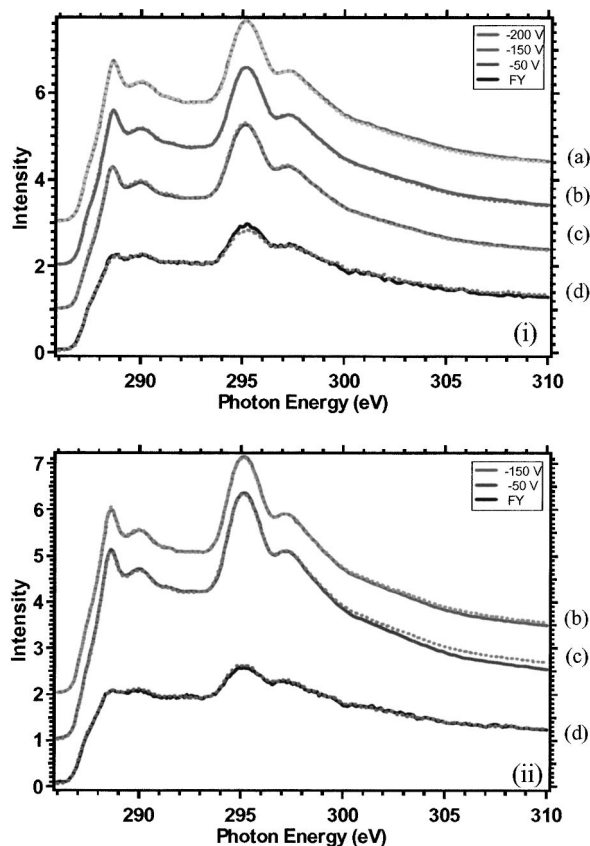


FIG. 4. NEXAFS carbon *K*-edge spectra for blends of PNBHFA with P(TBTFMA-NBHFA); (i) 50:50 thin film and (ii) 50:50 with 5% DTBPIP-FOS. Solid lines are electron yield spectra at (a)  $-200$  V; (b)  $-150$  V, and (c)  $-50$  V detector bias, and (d) fluorescence yield spectra. Dashed lines show fits to the data. Spectra are vertically offset for clarity.

sition. This is in contrast with the thicker 50:50 blend film that had an 18% PNBHFA surface composition. This difference arises because there is less material available in a thinner film to segregate to the photoresist/air interface. It is possible that one of the constituent polymers also prefers to wet the photoresist/substrate interface. As a result, there is considerable disparity between the film surface spectra and that of the bulk.

In the spectra shown in Fig. 4(ii), the PAG has segregated to the blend film surface and as a result the linear combinations based on the neat polymers alone are inadequate to fit the data. The 50:50 blend film containing 5% PAG was fit with 22% surface composition of PNBHFA, compared to 18% found for the 50:50 blend film without PAG. This reduction in surface composition of copolymer is manifested in a diminished peak at 288.5 eV corresponding to the  $C\ 1s \rightarrow \pi^*_{C=O}$  transition and can be attributed to the absence of any  $C=O$  bonds in the PAG molecule. While segregation of this PAG has been shown to occur in other photoresist systems,<sup>4,6</sup> it has not been found to affect dissolution of these blend films during development.<sup>5</sup>

Although it has been shown that the protected copolymer preferentially wets the surface of the blend film, the deprotected version of the copolymer has been shown to have a

lower water contact angle ( $59^\circ$ ) than the homopolymer.<sup>5</sup> Consequently, it is expected that partially deprotected P(TBTFMA-NBHFA) will have comparable wetting characteristics and dissolution behavior compared to the PNBHFA homopolymer. However, it is important to further investigate the implications of this surface segregation and formation of a wetting layer in order to anticipate issues that may arise in the line edge region.

#### IV. SUMMARY

The chemical composition of the surface and bulk chemistry of various blend compositions of model 157 nm photoresists were investigated with NEXAFS. It was shown that there is significant segregation of the P(TBTFMA-NBHFA) copolymer to the surface of the blend films. The resulting surface composition was far in excess of the composition of the copolymer in the blend, particularly when the copolymer was the minority component. This information suggests that substantial surface effects related to the relative surface energy of the constituent polymers and other additives occur in this blend formulation. This segregation can take place during normal photoresist processing, particularly during the spin coating and baking steps.

#### ACKNOWLEDGMENTS

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