Chemical mapping of polymer photoresists by scanning
transmission x-ray microscopy (STXM)

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Abstract

Scanning transmission x-ray microscopy (STXM) is shown to be a powerful imaging technique that provides chemical selectivity and high spatial resolution (~35 nm) for studying chemically amplified photoresists. Samples of poly(4-t-butoxycarbonyloxystyrene) PTBOCST resist, imprinted by deep ultraviolet lithography with a line/space pattern of 1.10 µm/0.87 µm followed by a post-exposure bake, are used to demonstrate STXM imaging capabilities to extract photoresist latent images. Chemical contrast in the image is obtained by measuring the absorption of the x-ray beam at an energy of 290.5 eV, corresponding to a carbon K shell electrons transition to the unoccupied π* molecular orbital of the carbonyl group. A quantitative analysis provides the spatial distribution of the fraction as well as the thickness of the unexposed and deprotected polymers remaining after the post-exposure bake stage. Advantages and limitations of STXM in comparison with other imaging techniques with chemical specificity are discussed.
I. Introduction

The continuing increase of integrated circuit performance is largely based on the capability of advanced lithographic techniques to pattern resist materials with sub-100 nm line dimensions.\textsuperscript{1-5} With decreasing feature sizes, new demands are placed on measurement characterization techniques at different stages of pattern formation.

The process of transferring a pattern to semiconductor surfaces by chemically amplified resist lithography consists of several steps. A latent image is first created by exposing the photoresist to short-wavelength (typically UV) radiation through a patterned mask. For test patterns, interferometric lithography can also be used to create a sinusoidal standing wave pattern produced by interference at the region of intersection of two coherent light beams.\textsuperscript{6} An acid species is produced in the photoresist (an acid-labile polymer blended with a photo acid generator) only in the regions exposed to radiation, creating a first latent image. The exposure stage is followed by a complex reaction-diffusion process that takes place during a post-exposure bake (PEB) at elevated temperatures. During the bake the acid diffuses and interacts with multiple reaction sites to catalyze deprotection, which alters the chemical and physical properties of the polymer. These chemical changes provide routes to investigate polymer photochemistry and measure line dimensions of latent images at this important intermediate stage in the image formation. The final step is the development of the latent image by dissolution of either the deprotected (positive tone resist) or unmodified polymer (negative tone resist) areas followed by selective etching of the underlying semiconductor wafer in the regions where the polymer was removed.
Of primary importance for controlling line dimensions in the sub-100 nm range is the direct measurement of the spatial evolution of the reaction-diffusion front. To achieve this goal, techniques are needed with both good chemical sensitivity and very high spatial resolution. Fluorescence microscopy is used to characterize polymer photoresists through specific labeling with pH sensitive dyes. The disadvantage of this technique is that it requires fluorophores that may affect the parameters of acid diffusion and reactivity and, consequently, the line dimension/edge roughness. Optical microscopies that probe the vibrational absorption band changes occurring during UV exposure and PEB circumvent this drawback of labeling. Infrared near field scanning optical microscopy (IR NSOM) is used to selectively probe the OH vibration produced upon the acid catalyzed reaction in certain resist systems. Images with chemical contrast (due to selective absorption) were obtained with a spatial resolution of 300 nm at 3µm (the OH stretching vibration) along with a simultaneous topographical image. Considerably higher spatial resolution is expected to be achieved by apertureless near field scanning optical microscopy when used with infrared absorption contrast. However, this technique is sensitive only to near-surface regions. The method also faces significant challenges in detecting the small signal (light scattered from the tip) in the presence of a large background. To alleviate this difficulty, which is inherent to the method’s principle, polarization-based differential interferometric detection along with background subtraction techniques such as lock-in detection at higher harmonics have been used. Application of spontaneous Raman scattering spectroscopy is also limited by low sensitivity, due to the small Raman scattering cross section, which thus requires long integration times. This low sensitivity is overcome by coherent anti-Stokes Raman scattering (CARS) microscopy, which has
proven particularly useful for imaging of living cells.\textsuperscript{16-19} CARS microscopy is used for imaging polymer photoresists by probing the carbonyl stretching vibration in samples of poly(tert-butoxycarbonyloxystyrene).\textsuperscript{20} The much stronger signals in CARS microscopy yield chemical images based on Raman contrast within tens of seconds, making CARS very attractive for fast imaging and even real time investigations of photoresists. Depth profiling due to the laser beam focal volume is also possible. Using CARS, chemical images of polymer photoresists were obtained with a spatial resolution of approximately 270 nm.

In addition to optical imaging techniques, scanning transmission electron microscopy (STEM) provides excellent spatial resolution but typically does not have sufficient chemical sensitivity beyond the elemental level. In addition, there is a high rate of radiation damage in polymers due to the energetic electron beams.\textsuperscript{21}

Using complementary x-ray and neutron reflectivity measurements, non-imaging techniques can detect the spatial evolution of the reaction-diffusion process in chemically amplified photoresists with extremely high resolution (in the range of a few nanometers). These complex measurements yield compositional and density profiles through isotopic labeling.\textsuperscript{22}

In this paper, we explore the potential of scanning transmission x-ray microscopy (STXM) for the rapid chemical imaging of polymer photoresists. STXM,\textsuperscript{23-26} currently a synchrotron radiation soft x-ray based technique, has advanced rapidly in the last decade. The short acquisition times as well as the availability of experimental set-ups that enable measurements of samples placed in heating cells and under chemical exposure, make STXM a very attractive imaging technique for studying photoresists, in particular due to
its potential for studying the reaction-diffusion process during real time baking. Furthermore, the quantitative chemical mapping of the relevant chemical species provides important information about the spatial extent of the deprotection reaction. In this study, we demonstrate the chemical sensitivity of STXM by examining line patterns in poly(tert-butoxycarbonyloxystyrene) (PTBOCST) polymer photoresists at the carbon K edge.

II. STXM technique

a) Achieving high spectral resolution

Since the STXM method has not been applied to analyze patterned polymer photoresists, a brief description of the basic method of scanning transmission x-ray microscopy is provided here.

The absorption of x-rays passing through the sample depends on the nature of the substance, the thickness of the sample and the density of absorbent centers. Photon absorption can cause excitations of inner shell electrons to unoccupied energy levels or can remove the electron completely to generate an ionized atom or molecule. Traditionally, x-ray absorption was described in terms of absorption edges, i.e. the onset of inner shell ionization at specific energies for each atom. With the advent of tunable x-ray sources from synchrotron radiation facilities, x-ray absorption spectroscopy became a powerful technique in chemical analysis extending its capabilities beyond providing elemental composition to also providing chemical bonding information. This is due to the increased spectral resolution of soft x-rays produced at synchrotron facilities (~0.1 eV or better) in comparison to the spectral resolution obtained with hard x-rays (~1 eV). The sharp spectral features observed close to the absorption edge are referred to as ‘near edge
x-ray absorption fine structure’ (NEXAFS).\textsuperscript{27, 28} These features, which can be much stronger than the absorption edge change itself, correspond to transitions of the inner-shell electron to unfilled molecular orbitals or conduction bands. As the x-ray energy is increased throughout an absorption edge, the first observed structure is often associated with the lowest unoccupied molecular orbital, a $\pi^*$ orbital for unsaturated molecules (double or triple bonds), followed by transitions to higher energy unoccupied molecular orbitals, typically of $\sigma^*$ character associated with saturated (single) chemical bonds, and finally direct inner-shell ionization.\textsuperscript{23, 24, 27} This fine structure is determined by the geometric and electronic bonding structure of the sample. NEXAFS spectra can be significantly different even for similar chemical compounds. Hence, NEXAFS spectra can often be used as a fingerprint for distinguishing between very similar compounds. We use this capability in the following sections to distinguish between the initial and chemically-transformed polymer photoresist materials.

\textbf{b) Concept of STXM}

The incident synchrotron soft x-rays are monochromated, then focused to a diffraction-limited spot (typically 35 nm) by a Fresnel zone plate. Images are obtained by measuring the intensity of the transmitted x-rays as the sample is raster scanned through the focused beam. Spectra are recorded in point, line or image mode by acquiring signals at multiple photon energies. Spectra at each pixel are measured by recording images as a function of x-ray energy. Images at different energies are acquired individually, or in a stack mode, where the software automatically changes the energy in specified steps and records an image. In the stack mode there are more options available for processing the data (such as the alignment of images at different energies). The signal converted to
optical density (OD), is sensitive to sample thickness, density and composition, according to the following equation:

$$OD = -\ln \left( \frac{I}{I_0} \right) = \sigma t = \mu \rho t$$  \hspace{1cm} (1)

Where $I_0$ is the incident photon flux intensity, $\sigma$ is the linear absorption coefficient, $t$ is the thickness, $\mu$ is the mass absorption coefficient and $\rho$ is the density. With too little absorption (sample too thin), the signal is lost in the noise. If the absorption is too high, then various artifacts dominate the observed signal, and the signal loses quantitative accuracy. Normally, the range of OD is from 0.1 to 3. All samples in this study had optical densities < 1.5. For carbon studies in organic materials, samples need to be between 50 and 300 nm thick, which is well-matched to novel polymer photoresists that will be used in the future.

**III. Experimental methods**

The STXM’s used were at beamlines 5.3.2 and 11.0.2 of the Advanced Light Source (ALS). Beamline 5.3.2 is a horizontal dispersive bending magnet beamline, optimized for an energy range from 250 eV to 600 eV, which covers C 1s, N 1s and O 1s absorption edges (particularly important for polymer chemistry). However the usable photon range is considerably higher, at least from 200 eV to 1200 eV. The beam is monochromatized by a spherical grating optimized at C 1s to give an energy resolution of 100 meV. A detailed description of the STXM at 5.3.2 has been published.\(^{29}\) Beamline 11.0.2 is an undulator beamline optimized for an energy range from 200 eV to 1900 eV and operates with a plane grating monochromator consisting of a double ruled grating, with 150 lines/mm and 1200 lines/mm. Beamline 11.0.2 has a much higher flux due to the insertion device (elliptically polarizing undulator), hence more care is necessary to
prevent radiation damage. This beamline has the potential of providing higher spectral resolution and the possibility of controlling the polarization of the x-ray beam.

The schematic layout of the STXM is shown in Fig. 1. The x-ray beam exits the beamline through a 50 nm thick Si$_3$N$_4$ window, which isolates the STXM chamber from the ultrahigh vacuum of the beamline. The beam is focused by a Fresnel zone plate (provided by the Center for X Ray Optics) to a diffraction-limited spot that gives the spatial resolution of the microscope, which for these experiments was typically 35 nm.$^{30}$ To eliminate undesired diffraction orders at the sample, the zone plate is fabricated with a beam stop at its center. The filtering of the first order diffracted light is achieved by an order selective aperture (OSA), optimally positioned, in combination with the central stop of the zone plate. The diffraction-limited spatial resolution for a fully coherent beam is determined directly by the width of the most outer zone of the zone plate. Zone plates are achromatic lenses with a focal length proportional to the photon energy. Thus, during the acquisition of NEXAFS spectra or an image-sequence at many photon energies (referred to as ‘stacks’), the STXM is refocused synchronously as the photon energy changes. Depending on the focal properties of the zone plate used, this requires motions over 150-200 µm for a 30 eV wide C 1s NEXAFS scan, or even greater (> 1 mm) for changes between different absorption edges. The STXM’s used in this work use interferometer control that allows low distortion imaging and the precise measurement of the transverse position of the zone plate relative to the sample with a precision of 2.5 nm.$^{30}$ Due to the challenges in scanning x-ray optics, samples are typically scanned relative to the stationary x-ray beam. The sample is scanned using a two-axis x, y piezoelectric stage that provides fine motion over a limited field of view. To provide motion in the range of
millimeters, this x, y piezo stage is mounted on top of an x, y, z stepper motor stage. The transmitted x-ray intensity is measured by using a phosphor (fine grained powder on fiber optic) detector that converts x-rays to visible light. The visible light is detected by a high performance photomultiplier (PMT) with count rate capabilities in the tens of MHz. The software used to process the data is AXIS 2000.

Photoresist samples consist of thin films of poly(4-t-butoxycarbonyloxystyrene) (PTBOCST) patterned with an unequal line/space pattern having a total period of ~1.97 µm (see below). The concentration of the photoacid generator (PAG) in the resist, bis(4-t-butylphenyl)iodonium perfluorobutanesulfonate), was 0.045 mol/kg solids. The pattern was written using UV light through a 100 nm thick chromium on quartz contact mask with measured opaque chromium regions of ~1.10 µm at the top and 1.26 µm at the base and open spaces with corresponding dimensions of 0.87 µm (top) and 0.71 µm (base), respectively. The samples were prepared by coating the resist on 1 inch diameter polished sodium chloride plates followed by a post-apply bake at 130 °C for 90 s. Following exposure to UV light (10 mJ/cm² at 254 nm for patterned samples, 100 mJ/cm² at 254 nm for blanket exposed control samples), films were post-exposure baked at 100 °C for 90 s. Under acidic conditions, the tert-butoxycarbonyl group is converted to a hydroxy group with release of carbon dioxide and nominally iso-butylene as well as other volatile by-products, as indicated in the chemical formula presented in Fig.2. The release of the reaction by-products in the exposed regions causes the polymer to shrink, generating a topographical pattern. To lift the polymer off the substrate and mount it for STXM studies, the substrate was then placed in a shallow dish containing deionized water. After approximately 15 minutes the sodium chloride substrate dissolves and the films float to
the surface. These films are placed onto copper TEM grids for the STXM measurements. Small holes in the polymer film, usually present due to preparation procedures, are used to measure the incident photon flux intensity for normalization.

**IV. Results and Discussion**

Figure 3 shows carbon edge NEXAFS spectra of the unexposed PTBOCST polymer and of its UV-exposed and deprotected form. Both spectra display a prominent isolated sharp peak at 285.3 eV, arising from the carbon 1s→π* transition in the C=C bond. The shoulders between 287 and 290 eV are due to 1s→σ* transitions from carbon in CH, CH₂ and CH₃ bonds. The prominent peak at 290.5 eV in the unexposed PTBOCST that disappears after the deprotection reaction is attributed to the C 1s→π* transition of the C=O molecular orbital in the tert-butoxycarbonyl group. This particular spectral feature enables chemical contrast in the PTBOCST photoresist to be imaged and quantified. The peak at 287.1 eV, which becomes more prominent in the spectrum of the deprotected polymer, is presumably due to the formation of the phenolic OH group.¹¹ Figure 4 depicts images taken at three different energies of a PTBOCST polymer film patterned with the nominal line/space pattern described above. At each photon energy the sample is scanned laterally through the x-ray focus yielding a transverse xy image of the polymer film. The dwell time in Fig. 4 is 1.6 ms per 50 nm pixel. The acquisition time for one 10 µm x 10 µm image (not displayed fully in Fig. 4), at this dwell time, is 8 min. The 50 nm distance per pixel was chosen to reduce radiation exposure while maximizing the spatial resolution. The spatial resolution of the microscope has been tested on samples with patterns of lines/spaces fabricated in gold with electron beam lithography techniques.
and supported on Si₃N₄ membranes. Lines with dimensions as small as 35 nm are resolved by using a similar zone plate that has a 40 nm outermost zone width. Figure 4a shows an image obtained at 290.5 eV. The dark region (zero absorbance) in the lower right hand corner is due to a hole in the sample. Such holes are used to measure the incident photon flux intensity, I₀ which is necessary to convert the intensity measured through the polymer sample into optical density. Topographical features contribute to the total contrast in STXM images due to the direct proportionality between the x-ray absorption and the number of absorptive centers. In these experiments the number of absorptive centers decreases following the deprotection reaction in the exposed regions due to the release of volatile carbon-containing by-products. Figure 4b shows an image at 314.5 eV where the main contribution to the contrast originates from this topographical (thickness) difference of our samples. However an image at 280.0 eV, which is below the onset of the C K edge, displays no such contrast (Fig. 4c).

A one dimensional profile obtained by averaging along the longitudinal direction of the line pattern, obtained by summing the lines in the image at 290.5 eV and plotting along the transverse direction of the pattern, is presented in Fig. 5. The estimated contrast from the line profile, using the formula \( \frac{I_{\text{max}} - I_{\text{min}}}{\frac{I_{\text{max}} + I_{\text{min}}}{2}} \), is \((32.6 \pm 1.1)\%\). \( I_{\text{max}} \) (\( I_{\text{min}} \)) is the maximum (minimum) optical density measured in the one dimensional profile. The image contrast at 310 eV, which originates primarily from the topographical contribution is \( \approx (14.1 \pm 1.5)\% \). The difference of about \((18.5 \pm 2.6)\% \) represents the desired chemical contribution to the total contrast of the image recorded at 290.5 eV. The uncertainties were estimated as 0.06 for \( I_{\text{max}} \) and 0.02 for \( I_{\text{min}} \). Part of this uncertainty arises from small variations in the initial sample thickness. The chemical map at 290.5 eV
is important in this study since it exhibits the advancement of the direct chemical changes produced by the deprotection reaction. Furthermore, a quantitative spatial distribution of the deprotected polymer after post-exposure bake determines the quality of the pattern transfer during the dissolution step, since dissolution is directly related to the percentage of carbonyl bonds that have been transformed by the deprotection.  

The quantitative mapping of the carbonyl group can be obtained with the least squares method by determining the coefficients \( a_{\text{PTBOCST}}^{x,y,n} \) and \( a_{\text{PHOST}}^{x,y,n} \) in the following equation that minimize the quantity \[ \left( OD_{\text{measured}}^{x,y,n} - OD_{\text{calculated}}^{x,y,n} \right)^2: \]

\[
OD_{\text{calculated}}^{x,y,n} = \text{const}_{n} + a_{x,y,n}^{\text{PTBOCST}} \cdot OD_{\text{PTBOCST},n}^{x,y,n} + a_{x,y,n}^{\text{PHOST}} \cdot OD_{\text{PHOST},n}^{x,y,n} 
\]

where \( OD_{\text{measured}}^{x,y,n} \) is the optical density at each pixel \((x,y)\) of the recorded images at different energies \(1\ldots n\) in the measured stack, \( OD_{\text{PTBOCST},n} \) and \( OD_{\text{PHOST},n} \) are reference spectra of the pure polymers (PTBOCST (unexposed) and (PHOST) deprotected). The measured spectrum at each pixel is thus a linear combination of reference spectra of pure polymers and the linear coefficients are quantitative measures of each pure component at each position. If the reference spectra are in OD from polymer films having the same thickness as the corresponding regions of the patterned sample, then the coefficient \( a_{x,y,n}^{\text{PTBOCST}} \times 100 \) represents the fraction of unexposed polymer at each position measured as a percentage. Similarly, \( a_{x,y,n}^{\text{PHOST}} \times 100 \) gives the fraction of the exposed and deprotected polymer at each position. Normally, \( a_{x,y,n}^{\text{PTBOCST}} \) and \( a_{x,y,n}^{\text{PHOST}} \) have values between 0 and 1 and at each pixel \((x,y)\) and their sum equals 1. However, due to measurement statistics, the coefficients can be less than zero or greater than 1. For example, if the OD of the reference is much weaker than that in an image of a sample of unknown composition,
then the coefficients can be higher than 1. The constant in Eq. 2 accounts for a difference in energy-independent scattering of the x-rays.

At 290.5 eV, $a_{x,y,n}^{PTBOCST}$ represents the spatial distribution of the carbonyl group, which we normally identify with the unexposed polymer. If the reference spectra are scaled per unit thickness (representing OD per one nm thickness), using the atomic scattering factors, then the linear coefficients are obtained in units of nm and their maximum values (occurring in the corresponding centers of each polymer region) represent the thickness of the unexposed and post-exposure deprotected areas at the centers of each polymer. By using this procedure we estimated the thickness of the unexposed and deprotected regions to be approximately 130 nm and 100 nm, respectively. These values are in agreement with the thickness values estimated in the process of fabrication of the polymer films. Figure 6 presents the quantitative map profile of the unexposed and post-exposure deprotected polymers and shows what percentage of the initial PTBOCST polymer is converted into the deprotected form, PHOST, at each position in the imaged pattern.

Figure 5 shows that the photo treatment and the chemical changes during the high temperature bake have imprinted lines of nominal width of ~ 0.6 µm corresponding to the valleys, whereas the unexposed regions corresponding to the peaks are wider (~ 1.1 µm). The same dimensions of the line pattern are displayed by the quantitative map of Fig. 6. The exposed regions of the polymer appear to be slightly narrower than the open areas measured on the mask, while the dimension of the unexposed areas is consistent with the measured dimension of the opaque regions of the mask. A possible explanation for this difference in the exposed line dimensions can be the physical volume shrinkage.
of the film upon deprotection, which could manifest itself not only in thickness, but also in lateral dimension, particularly since the polymer is floated off the substrate. This might be suggested by the fact that approximately 40% volume shrinkage is expected to occur during the deprotection reaction, whereas only about 23% thickness shrinkage results from a quantitative analysis. Similar effects were also observed in chemical imaging of similar photoresists by optical techniques such as CARS microscopy\textsuperscript{20} and IR NSOM\textsuperscript{10,11}.

In imaging by IR NSOM, the narrowing of the valleys (the exposed regions of the polymer) was in part attributed to the limited reach of the probing IR light at the edges of the deep regions due to the conical shape of the tip.\textsuperscript{10,11} However, this is not the case in the present experiment which was done without a tip.

Both Fig. 5 and Fig. 6 show a weak periodic pattern superimposed on the profile of the unexposed regions. This has also been observed before in samples patterned by exposure through a mask and has been attributed to interference of light leaking under the mask into the unexposed regions.\textsuperscript{10} From the quantitative map (Fig. 6) most exposed regions contain about 10% ± 5% of the initial carbonyl groups present even in the center region of the line, while fewer exposed regions show complete deprotection. The presence of carbonyl groups in the exposed area suggests that the deprotection reaction is not complete throughout the exposed regions. Furthermore, the small reminiscent peak at 290.5 eV, which is attributed to the carbonyl group and was confirmed in the measured oxygen spectra, does not completely disappear in the spectrum of the fully exposed region of the photoresist (Fig. 3b). Either the deprotection reaction is not complete, or residual carbonyl species are not released and remain trapped in the polymer matrix.
Chemical changes between the exposed regions of the patterned photoresist and the non-exposed regions include loss of a carbonyl group and the formation of a phenolic OH group. In addition, the fluorine containing photoacid generator may decompose or diffuse, creating a spatial distribution of the photoacid generator. Both of these regions offer additional opportunities to probe the polymer chemistry by STXM. Experiments to measure pure chemical contrasts at the oxygen K edge (525-550 eV) and the fluorine K edge (680-710 eV) would in principle provide important complementary information to the carbon edge region. Contrast images (due to differences in sample thickness between the exposed and unexposed regions) were observed at both the fluorine and oxygen edges and displayed line/space dimensions consistent with those observed at the carbon edges. The signal to noise observed in the oxygen spectra was weaker than that observed at the C K edge. Therefore we did not attempt chemical quantification at the oxygen K edge. Absorption (~532.7 eV) corresponding to the O 1s \( \rightarrow \pi^* \) transition in the carbonyl group\(^{31}\) was observed in both the spectra of the exposed and unexposed regions of the patterned photoresist. The appearance of a small shoulder at ~535.7 eV in the exposed sample, is probably due to the 1s\( \rightarrow \sigma^* \) transition of the C-O in the alcohol group formed upon deprotection. We were unable to identify a fluorine spectrum from these samples. This could be due to the low acid concentration combined with a homogeneous distribution of the acid.

The achievement of high spatial resolution, by focusing the x-ray beam to a spot (~ 35 nm), is however fundamentally limited by radiation damage due to the high energy deposition into a small volume. Radiation damage is primarily manifested by breaking of chemical bonds and loss of mass.\(^{34}\) At the same time, in acid catalyzed photoresist
chemistry, the x-ray radiation can also initiate the acid catalysis reactions, which in the case of PTBOCST photoresist depletes the polymer of the carbonyl group. The decrease in bond density will be manifested as a decrease in the corresponding peak heights in the NEXAFS spectra. Basic considerations of image contrast, spatial resolution and radiation damage have to be correlated in choosing the exposure parameters. Acquisitions of images at a large number of energies are particularly subject to radiation damage compared with the acquisition of a single image. Figure 7 shows an example of radiation damage produced by making an x-ray line scan perpendicular to the original line pattern of the sample. The line scan is recorded in the energy range from 275 eV to 320 eV in steps of 0.4 eV with a dwell time of 3 ms per 10 nm scan distance. The repeatedly irradiated line (scanned about 110 times) has the same appearance and has the same spectrum (data not shown) as the deprotected regions of the photoresist due to the depletion of C=O bonds. Considering an average photon flux of about $10^6$ photons/s at an average photon energy of 300 eV, the estimated integrated exposure dose is about 20 J/cm$^2$. The actual irradiation dose applied in this scan is higher by a factor of ~3 due to timing overhead in scanning a diagonal rather than a horizontal line. The resulting exposure dose is about 180 times higher than a typical exposure dose used for UV patterning of photoresists. Further experiments, where a reduced number of images in a stack were taken, and with typical dwell times of about 1 ms per 50 nm pixel size, showed no observable radiation damage in PTBOCST samples. For a dwell time of 1 ms per 50 nm scan distance, the radiation exposure at an average energy of 300 eV, with an average photon flux of $10^6$ photons/s, in recording a stack at 5 energies is 10 mJ/cm$^2$. This is 10 times smaller than a typical irradiation exposure dose used in UV patterning of
photoresists. However, due to the different interactions of the UV and x-ray radiation with the samples, a direct comparison between x-ray and UV radiation may not be relevant.

Summary

In this study, we have used STXM as a potential technique for investigating chemically amplified photoresists. Chemical imaging of polymer photoresists using STXM offers several advantages over existing optical techniques employed. Similar to optical techniques such as IR NSOM, spontaneous Raman microscopy and CARS, STXM achieves chemical selectivity without the use of fluorescent contrast agents. As shown in this preliminary study, power of chemical imaging using STXM is primarily based on its spatial resolution, which exceeds that of the other spectroscopic techniques, in addition to quantitative measurements of the chemical components at each volume position in the sample.

We measured the spatial distribution of the carbonyl fraction remaining after the post-exposure bake stage with a spatial resolution of 35 nm. This information reveals the effectiveness of the deprotection reaction at different positions in the patterned sample and can be used to theoretically predict the pattern after the dissolution step. Furthermore, the quantitative analysis independently estimates the thickness of the two regions of the patterned photoresist.

STXM offers the possibility of obtaining chemical images at very high spatial resolution in just a few minutes and can be adapted to a wide range of sample environments, such as magnetic fields, variable temperature, and aqueous media for polymeric and environmental samples. Furthermore, the near edge x-ray absorption
cross section is polarization dependent. The resulting x-ray linear dichroism can be used to image the orientation of specific bonds in (partially) ordered samples.

In contrast with the microscopy techniques previously used for imaging photoresists, STXM offers a unique opportunity to study the spatial evolution of the reaction–diffusion process in real time. By choosing an adequate exposure dose, the soft x-ray beam can be used to generate an acid species and initiate the deprotection reaction under controlled heating. The advancement of the reaction front can be visualized by probing the changes in the x-ray transmission at different time intervals.

In conclusion, the chemical sensitivity of STXM allows imaging of polymeric photoresists with chemical contrast. STXM exhibits high spatial resolution and enables fast image acquisition rates. All of these aspects are key in investigating chemically amplified polymer photoresists, promoting STXM as a potentially powerful technique for studying these systems.

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References


Figure Captions

**Figure 1.** Schematic of the scanning transmission x-ray microscope (STXM).

**Figure 2.** Schematic representation of the deprotection reaction occurring during the post exposure bake.

**Figure 3.** (a) Carbon K shell NEXAFS spectrum of PTBOCST. The feature at 290.5 eV is attributed to the C 1s → π* transition in the carbonyl group. (b) Carbon K shell NEXAFS spectrum of the deprotected polymer, PHOST. Note the almost complete disappearance of the 290.5 peak as the polymer is depleted of the carbonyl group following the deprotection reaction.

**Figure 4.** Transverse xy images (absorption mode) of the patterned PTBOCST sample at (a) 290.5 eV, (b) 314.0 eV, and (c) 280.0 eV. Acquisition time of a 10 µm x 10 µm image (not shown fully) was 8 minutes, with a dwell time of 1.6 ms per 50 nm scan distance. The dark spot in the lower right hand corner is a hole in the sample where the incident photon flux I₀ is measured.

**Figure 5.** Line profile of the patterned PTBOCST sample obtained by averaging in the longitudinal direction of the pattern in the image shown in Figure 3a.

**Figure 6.** Spatial distribution of the fraction of carbonyl group (unexposed polymer): dotted line, and of the deprotected polymer: solid line, present after the post-exposure bake stage.

**Figure 7.** Transverse image (absorption mode) of a patterned PTBOCST sample damaged by repeatedly scanning of a line perpendicular to the patterned lines.
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