Chemical changes in hybrid photoresists
before and after exposure by *in situ* NEXAFS

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ABSTRACT

Due to its chemical specificity, the near edge X-ray absorption fine structure spectroscopy is an interesting technique to study the changes in hybrid organic-inorganic photoresists. In this work, we analyzed the chemical changes occurring in photoresists synthesized from organically modified precursors and transition metal alkoxides by sol-gel route. These systems are nonchemically amplified resists for ultraviolet, extreme ultraviolet, and electron beam lithography. They are based on Si, Zr, and Ti oxides or a combination of these. The experiments were conducted at the PolLux beamline of the Swiss Light Source, by a scanning transmission X-ray microscopy, which combines the spatially-resolved microscopy and fine structure spectroscopy at once. The absorption spectra were collected in the energy range of the carbon edge ($\approx$ 290 eV) before and after *in situ* exposure of the photoresists to 500 eV photons. The variations in peak intensity after exposure reveal the changes in the chemical environment of carbon and the chemical configuration of the organic ligands, regardless of the inorganic part. It was found that the photon exposure induced sizable photodegradation or photopolymerization of organic groups (phenyl or methyl methacrylate, respectively). These mechanisms contribute to the foundation for the exposure reaction in negative-tone hybrid photoresists. Interestingly, it was also found that the detachment of the phenyl ligand occurs in a variety of possible pathways to condensation. We believe that our results and approach can provide a better understanding of photochemistry of resists, in particular for extreme ultraviolet lithography.

Keywords: NEXAFS, STXM, organically modified precursors, organic-inorganic, X-ray absorption, organometallic, EUV, photoresist, hybrid

1. INTRODUCTION

Extreme ultraviolet lithography (EUVL) is set to become the technology of choice for high volume manufacturing of large scale integration devices. It represents a significant advancement because it uses light at extreme ultraviolet (EUV) wavelength of 13.5 nm, in comparison to the actual technology based on 193-nm wavelength. In order to realize EUVL, both industry and academia are making extraordinary efforts to design and produce exposure tools, optics, masks and photoresists[1]. The characterization of photoresists for EUV mostly focuses on the lithographic performance: sensitivity, roughness and resolution[2]. The understanding of the physico-chemical reactions that take place during photoresist exposure is still partly not understood. In particular, tracking the chemical changes occurring in a photoresist is considerably challenging even in the simplest molecules. In the case of photoresist, the characterization is usually done after exposure and after development. 'Flood' exposures are typically needed in order to enable the characterization over large areas by scanning electron microscopy, X-ray diffraction, secondary ion mass spectroscopy, and so forth. An additional hurdle is the time delay between exposure and characterization of the material (the latter, being usually done using different instrumentations and vacuum environments). As a consequence, adsorption and desorption can occur, as well as contaminations from ambient environment in the photoresist. All these reasons make characterization of thin photoresists films at the microscopic level difficult.

The near edge X-ray absorption fine structure (NEXAFS) spectroscopy exploits the photoexcitation of electrons from core shell to unoccupied molecular orbitals as a way to probe the atomic-specific chemical environment. Among other

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applications, this technique is appropriate to study the chemical properties in photodegradable materials, specifically those containing organic components. For instance, it clarified the exposure mechanism of PMMA both qualitatively (which carbon bond change) and quantitatively (how many)[3].

In recent years, a new class of photoresists has been attracting great interest for its technological applications. Negative-tone hybrid organic-inorganic photoresists are materials of interest in lithography, where they can be used as directly-patternable hard masks for pattern transfer into silicon substrates. During and after exposure, the organic component of the material is removed to leave behind a pseudo-glassy network with a high etch resistance. Owing to a remarkable combination of features (high resolution, high etch resistance, compatibility with existing process), hybrids are also interesting for applications in extreme ultraviolet (EUV) lithography, which is the next generation lithography for large scale integration[4]. The inclusion of metallic elements and/or high Z-number elements is a novelty in photoresist synthesis. In the specific case of EUV lithography, metal incorporation brings another great advantage of increased optical absorption; from the sensitivity standpoint, this advantage can offset the lack of chemical amplification. Indeed, absorption at EUV is entirely dictated by elemental composition. A recently adopted strategy is the incorporation in photoresists of those transition metals and metals or semimetals with large atomic number whose large *d* orbitals result in considerable interaction cross section with EUV photons. These considerations arise from the observation of the atomic absorption cross sections of elements from tabulated data and recent experimental findings[5,6].

In this work, we analyzed the chemical changes occurring in photoresists synthesized from organically modified precursors and transition metal alkoxides by sol-gel route. These systems are based on Zr, Si and Ti glassy oxide networks incorporating organic groups. Owing to its chemical specificity, NEXAFS has been demonstrated to be a powerful technique to analyze the chemical environment of the organic ligands of these organic-inorganic materials, regardless of the inorganic component[7]. Furthermore, the opportunity to measure the chemical changes shortly after exposure and *in situ*, prevents the photoresist from being exposed to environmental contaminations such as water absorption, desorption, and other radiations. It also brings the advantage of minimizing the exposure-to-measurement delay time. Energy-wise, the NEXAFS regime is focused on the absorption edge of carbon (290 eV), representing electronic transitions by photoexcitation of electrons of the carbon K-shell to higher energetic unoccupied (molecular) orbitals; whereas the extended X-ray absorption beyond the continuum level describes the electronic resonances of extended states in the continuum level further away from the excited element (Figure 1).
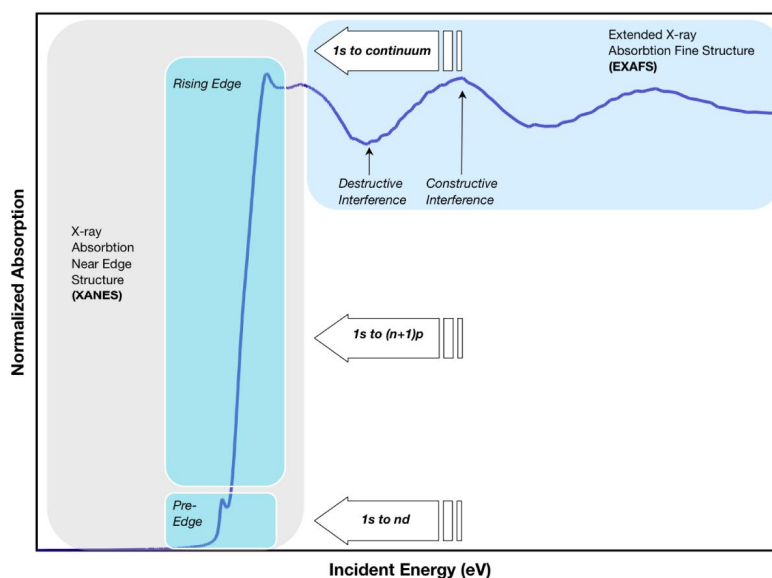

Figure 1. X-ray absorption provides information about electronic transitions by excitation of an electron from K-shell to unoccupied molecular orbitals (XANES or NEXAFS), and to other electronic resonances which extend to excitation energy beyond the continuum level (EXAFS).

2. EXPERIMENTAL DETAILS

2.1 Near edge X-ray fine structure spectroscopy

The experiments were conducted at the PolLux beamline of the Swiss Light Source, featuring a STXM (scanning transmission X-ray microscopy) which combines the spatially resolved microscopy and the NEXAFS spectroscopy at once[8]. In addition, the PolLux can also perform radiation damage study in photosensitive materials by *in situ* exposure to high photon flux. X-ray absorption spectra were acquired in the proximity of the carbon edge in the energy range 280-310 eV. The energy calibration of the beamline provides an accuracy better than 1 eV. The STXM exploits the focusing of the beam by Fresnel zone plate and enables the acquisition of X-ray absorption maps, spatially resolved to a resolution of about 100 nm. Although the spatial morphology is not of interest in the scope of this work (because spin coated photoresist films are not expected to have morphological features), the STXM made it possible to expose localized areas of the film and measure locally afterwards. To the purpose of the exposure, the beam energy was set to 500 eV. Despite the obvious differences between irradiating with 500 eV and EUV light (91.9 eV) or electron beam, the exposure *in situ* brings the advantage of keeping the sample in vacuum and preventing contaminations from ambient. Moreover, the selected photon energy is not matching any resonance of the material and, as a result, exposure determines the generation of photoelectrons in the material (similarly to what happens in lithographic processes carried out at energy above the ionization potential).

2.2 Samples synthesis and description

The hybrid organometallic photoresists were synthesized at University of Padua (Italy) by sol-gel chemistry: hydrolysis and condensation reactions occur at T<200°C ('chimie douce') as described elsewhere[9,10,11]. Materials were synthesized from organically modified precursors with network formers and/or network modifiers. The formers were alkoxides of the type $R_nSi(OR')_{4-n}$, with n = 1, 2. The schematic chemical structure is shown in the following Figure 2. The lithographic performance of these materials has also been assessed, by electron beam lithography, in previous works.
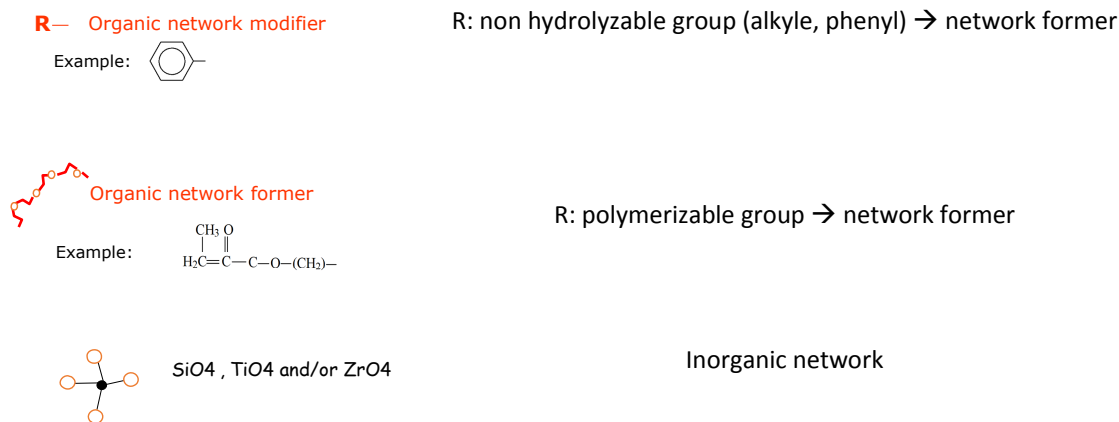

Figure 2. Schematic chemical structure of organic-inorganic photoresists.

After synthesis, these materials were spin-coated on thin silicon nitride membranes (≈ 100 nm thick), suspended on a silicon frame (≈ 280 μm thick). A post application bake, at 80 °C for 5 minutes, was carried out to remove the casting solvent from the film. The resulting, pristine, layer consisted of inorganic glassy network with covalently linked moieties, as shown schematically in the following Figure 3.
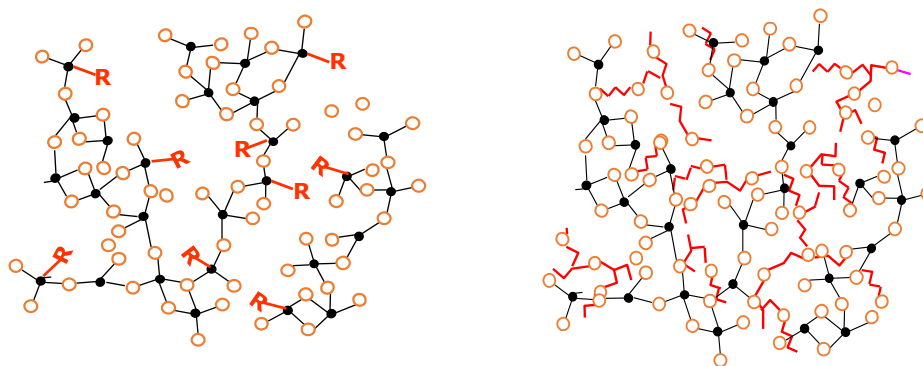
Figure 3. Two equivalent schematics of the chemical structure of the hybrid organic-inorganic photoresist before exposure. Symbols represent: silicon, zirconium or titanium (black circles), oxygen (orange open circles), organic groups (red 'R') and organic ligands (red solid lines).

The description of the hybrid network for the samples under investigation is given in Table I.

Table I. Samples description.

Sample	Type	Inorganic network	Organic ligand
S1	hybrid organic-inorganic	SiO_X	phenyl bridge
S2	hybrid organic-inorganic	$SiO_X + ZrO_X$	methyl methacrylate
S3	hybrid organic-inorganic	$SiO_X + TiO_X$	phenyl pendant

2.3 Quantitative fitting of absorption peaks

To clearly identify peak position and intensity, the measured NEXAFS spectra have been fitted to a combination of mathematical functions describe the physical response of soft X-ray absorption spectra of the materials in the given energy range. The physical mechanisms for soft X-ray absorption that have been accounted for were: 1) photoexcitation of a K-shell electron to unoccupied π^* or σ^* molecular orbitals; 2) photoexcitation of a K-shell electron to continuum states above the ionization potential (IP); and 3) decreasing absorption at energies in the extended structure. The fitting function of each energy spectrum was therefore a combination of: 1) sum of up to 9 symmetric gaussians; 2) normal cumulative function centered at energy equal to the ionization potential (IP); and 3) an exponentially decaying function. In summary, the fitting function is described by:

$$f(E) = \sum_{i=1}^{9} \left(\frac{1}{\sigma_i \sqrt{2\pi}} e^{-\frac{(E-\mu_i)^2}{2\sigma_i^2}} \right) + \frac{1}{\sigma_c \sqrt{2\pi}} e^{-\frac{(E-IP)^2}{2\sigma_C^2}} \times A e^{-\frac{E-IP}{\sigma}} \qquad \text{(Eq. 1)}$$

where the σ_i terms account for the width of the Gaussian; the μ_i terms account for the position of the Gaussian peaks; σ_c accounts for the continuum states; A and σ account for the magnitude and slope of the exponentially decaying term. A nonlinear-least-squares fitting to the experimental data was carried out by Levenberg Marquardt algorithm for all the data sets.

3. RESULTS AND DISCUSSION

On the pristine samples, the NEXAFS spectra were acquired while sweeping the beam over a wide area of material, using the STXM, to prevent undesired exposure of the photoresists. Afterwards, the energy of the beam was changed to

500 eV and the tool was set so as to increase the available flux and deliberately expose the material. Using the beamline focusing optics (Fresnel zone plate), exposure of the material was achieved over selected areas of about 1 μm diameter. As the material is poorly absorbing at that energy and because of the relatively low flux (in comparison to lithographic tools), exposure of even such a limited area required a considerable time (= 10 minutes) for lithographic standards. NEXAFS spectra were acquired again, after exposure, by using the STXM over the same exposed areas. The small scanning area (1 μm diameter) was not a limitation to the quality of the experimental data. It must be pointed out that the estimation for exposure doses cannot be straightforwardly calibrated against electron beam dose. Based on previous exposures on PMMA (not shown) carried out in the same experimental setup, the exposure dose for these samples was equivalent to at least 20 mJ/cm^2 (EUV wavelength) or 100 μC/cm^2 (electron beam). The experimental spectra and the quantitative fitting of the three samples before and after exposure are shown in Fig. 5.

The change in optical density (OD) of the materials after exposure was sizeable and allows us to draw some conclusions on the effect of exposure in these compounds. As a general consideration, the identification of NEXAFS peaks is not straightforward in complex macromolecules. To the purpose of identification and interpretation of the peaks, in the following we will refer to previous NEXAFS studies of organic compounds[3,12,13,14,15]. On the basis of the established knowledge, all samples show characteristic common features. The sharp isolated peak at ≈ 285 eV is clearly belonging to the π* C=C resonance of carbon-carbon double bond. The many overlapping peaks at 287-288 eV are not straightforward attributed. However, given the chemical composition, it is reasonable to associate them to resonances arising from carbon-hydrogen bonds (all samples) and C=O double bonds (S2 sample). The additional peaks beyond the step (i.e. above the ionization potential of the K-shell electrons) are indicative of C-C σ* resonances.

Notably, the spectra of the pristine S1 and S3 samples resemble the spectrum of benzene (also shown in Fig. 5a and 5e). This observation arises from the expectation that both compounds are synthesized to the purpose of having phenyl groups as organic ligands. After exposure, the spectra of the two samples change in different ways. In S3, the characteristic benzene peaks are preserved but have weaker intensity than in the pristine material. This finding might indicate that, after exposure, the phenyl pendant groups have either completely detached (and have been desorbed from the film) or are still wholly intact in the material. However, the intensity of the π* resonance in sample S1 is as high as in the pristine state (relative to the step height at the ionization potential). It can be conjectured that the bridged organic ligand in sample S1 requires a higher exposure dose to be removed with respect to system presenting phenyl in pendant configuration (sample S3). It is also possible that the exposure causes the phenyl ring to branch and form polyethyne chain. In the case of sample S2, the spectrum of the pristine sample closely resembles that of poly methyl methacrylate (shown also in Fig. 5c). The additional π* resonance of sample S2 at ≈ 285 eV should be again attributed to π* C=C resonance – which is missing in polymeric form of PMMA, but only in the monomer unit when attached as ligand. After exposure, the intensity of the 288 eV peak of the C=O double bond decreases significantly, which can be ascribed to the partial or total detachment of the organic ligand. To a first analysis, no other organic bonds form afterwards.
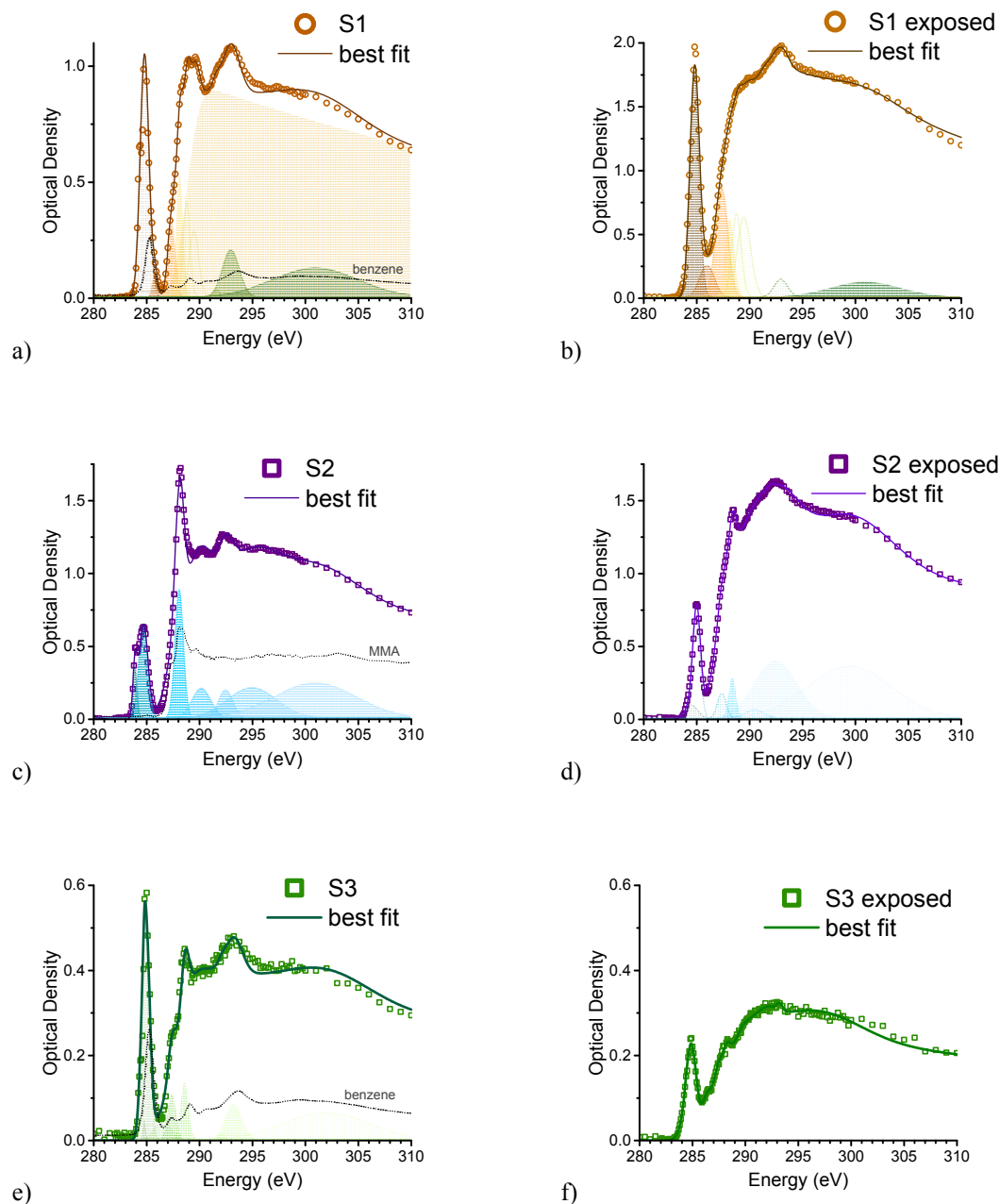
Figure 4. NEXAFS spectra (symbols) and best fit (solid lines) of hybrid organic-inorganic photoresist: samples S1 (a, b), S2 (c, d), and S3 (e, f), respectively before and after exposure. Shaded areas represent the individual components of the fitting function described in Eq. 1. For interpretation purposes, the NEXAFS spectra of benzene (a, e) and polymethyl methacrylate (c) are also shown (dotted black line).

In summary, it can be concluded that the effect of exposure to soft X-rays determines a modification of the organic component (partial or total removal or polymerization). It moreover enables the further growth and condensation of the inorganic network. The combination of these effects determines the mechanism according to which hybrid organic-inorganic photoresists are designed.

4. CONCLUSIONS

The NEXAFS has been demonstrated to be useful tool for the study of the chemical changes in hybrid organic-inorganic photoresists. We have exploited the high chemical selectivity of this technique to observe experimentally the change in the organic ligands, regardless of the contribution of the inorganic glassy network. By referring to established works from literature, we verified the chemical composition of the organic ligands as containing specific conjugated groups (either phenyl or methyl methacrylate). It was observed that relative intensity of the π^* C=C resonance (in the former) and of the π^* C=O resonance (in the latter) is a signature of the chemical changes in the organic part of the material after exposure. The exposure mechanisms proceeds by detachment of the phenyl component of the material and polymerization of the methacrylate group, promoting the formation of the oxide network, i.e. following the foundation for negative tone hybrid photoresist exposure.

5. ACKNOWLEDGEMENTS

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