ACS APPLIED MATERIALS & INTERFACES
Research Article
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Selective Fragmentation of Radiation-Sensitive Novel Polymeric Resist Materials by Inner-Shell Irradiation

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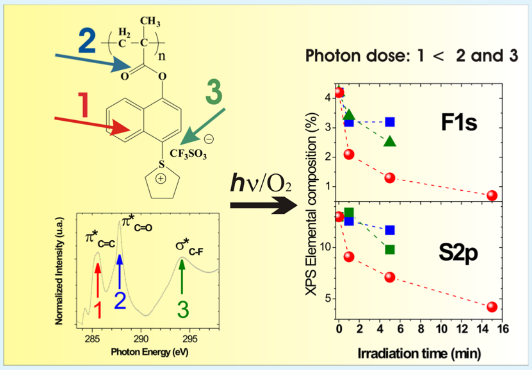
Supporting Information



ABSTRACT: Two key concepts in extreme ultraviolet lithography (EUVL) are important for it to be a candidate for the mass production of future integrated circuits: the polymer formulation and the photofragmentation process. In this work, both concepts were carefully studied. The design and synthesis of radiation−sensitive organic polymeric materials based on the inclusion of a radiation-sensitive tetrahydrothiophenium functional group are outlined. A 1-(4-methacryloyoxy)-naphthalene-1-yl)tetrahydro-1*H*-thiophenium trifluoromethanesulfonate (MANTMS) monomer containing the tetrahydrothiophenium group undergoes homo- and copolymerizations using free-radical polymerization with a 2,2′-azobis(isobutyronitrile) initiator. The surface photodegradation and oxidation of these novel polymeric materials were investigated using highly monochromatized soft X-rays from synchrotron radiation at the carbon K-edge excitation region. An efficient functionalization was observed when the excitation energy was tuned to C 1s → $\pi^*_{C=C}$. A high rate of defluorination and a loss of sulfonated groups as a result of an increase in the irradiation time for the MANTMS homopolymer thin films were mainly observed under the $\pi^*_{C=C}$ excitation of the naphthyl functional groups. On the contrary, excitation similar to C 1s → $\pi^*_{C=O}$ or C 1s → σ^*_{C-F} did not produce important degradation, showing a highly selective process of bond breaking. Additionally, the presence of methyl methacrylate copolymer in the original MANTMS yielded a much higher degree of stability against inner-shell radiation damage. Our results highlight the importance of choosing the right polymer formulation and excitation energy to produce a sensitive material for EUVL without using the concept of chemical amplification.

KEYWORDS: *synchrotron radiation, inner-shell excitation, nonchemically amplified resist, surface functionalization, EUV degradation*

INTRODUCTION

Extreme ultraviolet lithography (EUVL) is under consideration, as it is one of the promising candidates for next-generation lithography (NGL)[1,2] and is currently under extensive investigation as per the ITRS-2013 guidelines.[3] NGL technology is focused on the use of 13.5 nm (91.84 eV) wavelength radiation as a new excitation energy. However, radiation with a 13.5 nm wavelength is easily absorbed by most materials, including air, meaning that vacuum conditions are needed. Additionally, given the very stringent resist lithographic targets for resolution, line width roughness (LWR), sensitivity, and outgassing of resists[4] (EUV exposure can lead to reflective optics contamination), it is necessary to re-evaluate all the lithography processes starting with the current resist formulations.

Photons in the EUV region carry enough energy to break the chemical bonds of the polymers, simultaneously producing ablation and a high yield of secondary electrons.[1,5] As a result of the above high-energy processes, outgassing, morphological, and chemical changes in the polymer surface can lead to line edge roughness and pattern collapse, affecting resolution and the cross-sectional profile. Polymer resist composition is, as a result of the above challenges, a key issue in the development of NGL technology. Photoresists are mainly classified as chemically amplified resists (CARs) and nonchemically amplified resists (n-CARs). The CARs utilize acid-catalyzed reactions (deprotection or cross-linking) for the solubility switch and n-CARs use photoreaction to enable the solubility switch.[6]

We have previously reported the performance of n-CARs wherein an extensive evaluation of the photodynamics, i.e. fragmentation under EUV radiation, was conducted prior to EUV exposure for patterning.[7] Herein again, as a prelude to

Received: April 18, 2015
Accepted: July 9, 2015
Published: July 9, 2015

DOI: 10.1021/acsami.5b03378
ACS Appl. Mater. Interfaces 2015, 7, 16348−16356

patterning of the current polymers as EUV resists, we have similarly carried out a thorough evaluation of the EUV fragmentation of resists containing 1-(4-(methacryloyoxy)-naphthalene-1-yl)terahydro-1*H*-thiophenium trifluoromethanesulfonate. On the basis of these results, we will perform the patterning. The previously investigated novel n-CARs negative tone resists were based on the copolymer poly(4-(methacryloyloxy) naphthyldimethyl sulfoniumtriflate-*co*-methyl methacrylate) (MAPDST-*co*-MMA) and poly(4-(methacryloyloxy) naphthyldimethyl sulfoniumtriflate (MAPDST homopolymer) that were prepared from monomers containing sulfonium groups.[7,8] The combination of X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and quadrupole mass spectrometer (QMS) techniques allowed confirmation of the low stability of the triflate group, compared to the polymer backbone of the MAPDST homopolymer. Irradiation at 103.5 eV produced a high rate of evolution of gas fragments (SO_2^+, SO^+, and CF_3^+) that were efficiently detected by QMS. On the contrary, irradiation at the same energy of MAPDST-*co*-MMA showed that the copolymer was more resistant to radiation damage with a lower degree of degassing. This was attributed to the copolymer microstructure, where methyl methacrylate units replace the more volatile sulfonium moieties. From the obtained photodynamic data, it was concluded that fewer sulfonyl groups were affected in the copolymer under EUV exposure compared to the homopolymer.[7] Such higher resistance in the copolymer compared to the homopolymer formulation suggests the need for more fundamental studies to better understand the photodegradation and rearrangement processes of the resist under the high energetic conditions of soft X-ray irradiation.

Synchrotron radiation (SR) has very interesting properties for photochemical studies; it is highly monochromatic, it has an extremely high intensity, and the excitation energy can be tuned with high precision. Excitation of electrons from a particular atomic core orbital can be selectively adjusted by the photon energy to a specific resonant value that may lead to site-dependent molecular fragmentation. The probability of a specific core-hole to result in a particular fragmentation pathway will depend on the Auger transition rate to a suitable final state and the overlap between the molecular orbitals and the initial core-hole.[9] As the molecule becomes more complex, it would be expected that the site-dependent fragmentation becomes less pronounced in large molecules due to spreading of the overlap between the core-hole and the valence orbitals, but recent findings show strong site-dependency in complex molecules and polymers.[10−12] Hence, SR leads to significantly fast photodissociation processes where the constituents of radiative decomposition can accumulate in the near surface region of the polymer or can be oxidized in a later step.

SR also allows detailed characterizing of those chemical changes in situ using highly sensitive surface techniques, such as NEXAFS and XPS. Polymers containing fluorine in their structure have been studied over the years using SR, in an attempt to directly investigate the modification of the polymers during radiation exposure using core level spectroscopy. For instance, polarized NEXAFS studies of polyethylene and fluorinated polyethylenes were already studied by Ohta et al. in 1990.[13] Surface modification of poly(tetrafluoroethylene) (PTFE) by SR exposure has been the subject of many publications in the past,[14−19] including studies using several kinds of gas atmospheres to investigate the chemical changes after irradiation.[19] Okudaira et al. investigated the photodegradation of PTFE and poly(vinylidene fluoride) (PVDF) thin films by inner shell excitation.[20] Their results indicated that irradiation near F 1s and C 1s edges dissociate the polymer chain in C−C as well as C−F bonds. On the contrary, the same irradiation in PVDF produced mainly C−F and C−H bond scissions. Partial ion yields of the ions formed after irradiation for PTFE and PVDF films showed strong photon energy dependencies near fluorine and carbon K-edges; in particular, the excitation F 1s → σ^*_{C-F} transition was especially efficient for F^+ ion production for both polymers. In a recent study, PVDF films surface modification by inner-shell core level excitation was carried out by irradiation in the C 1s excitation region and also the irradiation dose.[21] The results showed a significant modification of the chemical content of the films and the electronic structure in the course of carbonization under synchrotron radiation. A gradual defluorination of the polymer was observed during irradiation. The authors concluded that the changes observed were the effect of two simultaneous processes: photochemical defluorination and diffusion of unbounded fluorine atoms to the sample surface.

In previous studies of polystyrene (PS)[12] and poly(sulfone)[22] thin films, we showed that the chemical composition of the irradiated films surfaces at selected inner-shell excitations can be tuned to produce selective surface functionalization. After the treatments, high oxygen surface concentrations were found in PS when specific K-shell excitations were selected. For example, the COO and CO elemental contributions in the PS surface measured by XPS reached a value higher than 70% when it was irradiated at a C 1s → σ^*_{C-C} transition. Recently, typical resists were investigated using monochromatized soft X-rays from SR, confirming that the sensitivity depends on the exposure wavelength[23] and also on the irradiation dose.[24] Resists containing some high absorption elements at the exposure wavelength showed high sensitivities.

A better understanding of the processes that occur after irradiation will in the future allow the right excitation energy to be chosen that will produce a selective surface modification of a polymer, keeping the bulk properties intact. We present here a detailed study of a carbon inner-shell excitation of a homopolymer and a copolymer that have sulfonium and triflate groups in their structures as EUV-absorption-enhancing units. The 1-(4-(methacryloyloxy)naphthalen-1-yl)tetrahydro-1*H*-thiophenium trifluoromethanesulfonate (MANTMS) and methacrylate copolymer (MANTMS−MMA) were irradiated at selected carbon inner-shell excitation energies, and the photodegradation processes were studied after oxidation of the surface under oxygen atmosphere. The main finding showed a highly selective process of bond breaking mainly under the $\pi^*_{C=C}$ excitation of the naphthyl functional groups.

■ EXPERIMENTAL SECTION

Materials. Tetramethylene sulfoxide, trifluoromethanesulfonic anhydride, and triethylamine (TEA) were purchased from Sigma-Aldrich and used as received. 1-Naphthol, methacrylic acid (MAA), and methyl methacrylate (MMA) were purchased from Acros Organics. Tetrahydrofuran (THF) was dried using a Na wire/benzophenone, and acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) were dried using calcium hydride (CaH_2). AIBN [azobis-(isobutyronitrile)] was purchased from Paras Polymers and recrystallized twice before using for polymerizations.

Procedure for the Synthesis of MANTMS Homopolymer. A 50 mL flask equipped with a magnetic stir bar was filled with 1.0 g (2.23 mmoL) of MANTMS monomer, 1 wt % AIBN, and 12 mL of acetonitrile under N_2 atmosphere. The mixture, after 1 h of N_2 purging, was left under magnetic stirring at 60 °C for 48 h under N_2 atmosphere. After completion, the reaction mixture was slowly poured into diethyl ether (50 mL), and the separated solid was washed with dichloromethane (DCM) and acetone. The resulting crude product was dissolved in methanol and then reprecipitated using diethyl ether. The separated pure product was filtered and dried in a temperature-controlled hot air oven at 50 °C for 1 day to yield 500 mg (50%) of a pale brown solid: ^{1}H NMR (500 MHz, MeOD-d_4) δ_H 8.24, 8.02, and 7.58 (6H, br peaks, ArH), 4.09 and 3.76 (4H, br peaks, SCH_2), 2.52, 2.42, and 2.19 (6H, br peak, CH_2−CH_2 protons of thiophenium ring and CH_2 polymeric), 0.87−1.90 (3H, br peak, CH_3 aliphatic); ^{13}C NMR (125 MHz, DMSO-d_6) δ_C 174.16 (C═O), 148.72, 131.57, 129.38, 128.33, 126.05, 124.62, 123.37, 121.96, 119.40, 117.43, 116.87 (aromatic, CF_3), 47.50 and 46.25 (SCH_2 and CH_2 polymeric), 28.62 (CH_2), 18.77 (CH_3); ^{19}F NMR (470 MHz; DMSO-d_6) δ_F −77.61 (3F, s, CF_3).

Procedure for the Synthesis of MANTMS−MMA Copolymer. MANTMS monomer (0.8 g, 1.78 mmol), methyl methacrylate (MMA) (0.2 g, 1.99 mmol), and AIBN (1% by weight, relative to both the monomers) were dissolved in a mixture of THF−CH_3CN (2:1) under N_2 atmosphere in a vial with a side arm, and the resulting solution was siphoned into the polymerization flask equipped with a silicone septum and a Teflon stirring bar. The mixture, after 1 h of N_2 purging, was left under magnetic stirring at 60 °C for 48 h under N_2 atmosphere. After completion, the reaction mixture was slowly poured into diethyl ether (50 mL), and the separated solid was washed with dichloromethane (DCM). The resulting crude product was dissolved in acetonitrile and then reprecipitated using diethyl ether. The separated pure product was filtered and dried in a temperature-controlled hot air oven at 50 °C for 1 day to yield 600 mg (60%) of a pale brown solid: ^{1}H NMR (500 MHz, DMSO-d_6) δ_H 8.22 and 7.56 (6H, br peaks, ArH), 4.27 and 4.08, 3.76 (7H, br peaks, OCH_3 and SCH_2), 2.34, 1.80, and 1.63 (6H, br peak, CH_2 polymeric and CH_2−CH_2 protons of thiophenium ring), 0.70−1.45 (3H, br m, CH_3 aliphatic); ^{13}C NMR (125 MHz, DMSO-d_6) δ_C 174.51 (C═O), 149.01, 132.53, 128.93, 124.98, 122.47, 119.91, 117.40, 116.07 (aromatic, CF_3), 76.23 (OCH_3), 52.54, 52.29, 48.04, and 46.47 (SCH_2 and CH_2 polymeric), 29.12 (CH_2), 19.42 (CH_3); ^{19}F NMR (470 MHz; DMSO-d_6) δ_F −77.61 (3F, s, CF_3).

Film Preparation and Inner-Shell Irradiation Study. Thin MANTMS homopolymer and MANTMS−MMA copolymer films (~100 nm thickness) were prepared inside a glovebox in a dry and inert atmosphere without UV exposure by the spin-coating technique from a ~10^{-4} mol/L chloroform solution. The films were cast on ~5 × 10 mm Si(100) wafers. Oxygen (99.999%) was used for surface oxidation during the experiments and was obtained from White Martins−Praxair, Inc. and used as received.

Synchrotron radiation (SR) experiments were carried out at the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil. The SGM (spherical grating monochromator) beamline, for VUV and soft X-ray spectroscopy (250−1000 eV), which gives a spectral resolution ($E/\Delta E$) better than 2000, was used as the monochromatic photon source. The experimental setup includes a computer controller XYZ sample manipulator housed in an ultrahigh vacuum (UHV) chamber with a base pressure of 10^{-7} Pa. The Si wafer substrates were directly attached to the sample holder by using conducting double-sided tape, and the SR beam was slightly defocused. No sample charging was observed throughout the experiments. Samples outside the UHV chamber were always manipulated in an inert atmosphere, and ultraviolet light exposition was avoided.

X-ray photoelectron spectroscopy (XPS) data were obtained using a high-performance hemispheric SPECSLAB II (Phoibos-Hs 3500 150 analyzer, SPECS) energy analyzer. The analyzer was calibrated against energy based on a photoelectron spectrum of Au $4f_{7/2,5/2}$ electrons. In recording high-resolution (HR)-XPS spectra, $h\nu$ was fixed at 850 eV for survey and F 1s, 650 eV for O 1s, and 500 eV for C 1s and S 2p signals. A pass energy of 50 eV was used for the survey spectra, whereas HR-XPS spectra of single core atom excitations were recorded with a pass energy of 10 eV. The C 1s signal (position of the C−C/C−H signals), 285.0 eV, was used for energy calibration. The HR-XPS envelopes were analyzed and peak-fitted after subtraction of the Shirley background, using Gaussian−Lorenzian peak shapes obtained from the CasaXPS software package.

Near-edge X-ray absorption fine structure (NEXAFS) spectra were obtained by measuring the total electron yield (electron current at the sample) simultaneously with a photon flux monitor (Au grid). The final data was normalized by this flux spectrum to correct for fluctuations in beam intensity.

When SR was used to functionalize the polymer surface, specific transitions were selected, and during a fixed period of time (1−15 min), the polymer was irradiated under UHV conditions. After irradiation, the samples were transferred to the UHV preparation chamber, and pure oxygen at atmospheric pressure was introduced for 30 min to neutralize the remaining radicals on the film surfaces. This treatment procedure was used for all the samples. Considering the collision frequency at a base pressure of 10^{-7} Pa and a sticking coefficient of unity, an oxidized monolayer is formed in ~10^4 s. As a consequence, the radicals, photogenerated at the surface during SR irradiation, remained until oxygen was introduced into the UHV chamber. XPS and NEXAFS spectra were obtained before and after irradiation.

RESULTS AND DISCUSSION

A new set of organic polymers, based on MANTMS or on a combination of MANTMS and methyl methacrylate (MMA) to increase the sensitivity toward the radiation, were prepared (Figure 1). The MANTMS monomer is the crucial part in designing a polymer containing tetrahydrothiophenium functionality at the first position of a naphthalene ring (see the Supporting Information for detailed reaction procedures and Scheme S1).

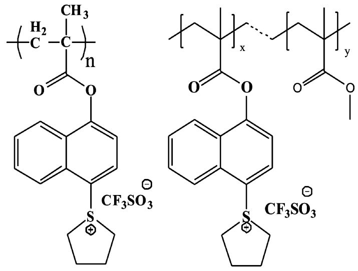


Figure 1. Chemical structures of radiation-sensitive organic polymers MANTMS homopolymer (left) and MANTMS−MMA copolymer (right).

Homopolymerization of the MANTMS monomer was initiated by 1 wt % AIBN in acetonitrile at a temperature of 60 °C under N_2 atmosphere for 2 days. The MANTMS homopolymer was obtained as a pale brown solid in 50% yield. The gel permeation chromatography (GPC) measurement showed an average molecular weight (M_w) of 15.04 × 10^3 g/mol with a polydispersity of 3.23 for this polymer. The MANTMS−MMA copolymer was prepared by using 80% MANTMS and 20% MMA monomers. The percentage of MANTMS and MMA monomers in the resulting copolymer was approximately 82% and 18%, respectively, which was calculated using ^{1}H NMR. Polymerization was carried out by a free-radical polymerization method using AIBN (1% by weight relative to both the monomers) as an initiator in a combined organic solvent of tetrahydrofuran (THF) and CH_3CN (2:1 ratio) at 60 °C under N_2 atmosphere for 2 days. The molecular weight of the synthesized copolymer was determined using GPC, and the M_w is 19.42 × 10^3 g/mol with a polydispersity of

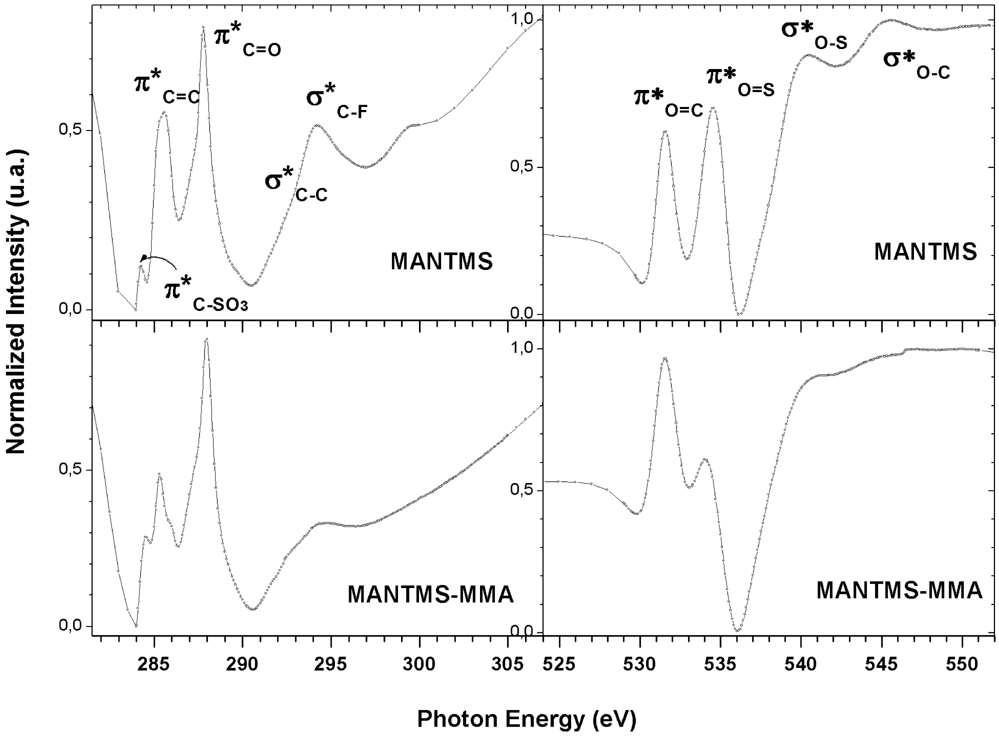


Figure 2. Carbon (left) and oxygen (right) K-edge NEXAFS spectra of untreated MANTMS homopolymer and the MANTMS−MMA copolymer showing the main inner-shell transitions involved (see the text for details).

3.66. The NMR spectroscopic characterization confirms the chemical structures of the newly synthesized polymeric materials, MANTMS homopolymer (**V**) and MANTMS−MMA copolymer (**VI**) (see the Supporting Information for more details). The thermogravimetric analysis (TGA) was used to investigate the thermal stability of the polymers (Figure S1, Supporting Information). The decomposition temperatures of MANTMS homopolymer (**V**) and MANTMS−MMA copolymer (**VI**) were 213.8 and 215.8 °C, respectively, measured at 5% weight loss.

Figure 2 shows the NEXAFS carbon and oxygen K-edge spectra of MANTMS homopolymer and MANTMS−MMA copolymer pristine thin films before irradiation. It is possible to attribute the main features in the C 1s absorption spectra as follows:[21,25,26] C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (287.7 eV), and C 1s → σ^*_{C-F} (294.1 eV). The wide signal at about 293.5 eV can be assigned to a typical C 1s → σ^*_{C-C} transition that it is overlapped by a main C 1s → σ^*_{C-F} transition.[20,21] Finally, a shoulder at about 284.4 eV can be ascribed to the C 1s(C−SO_3) → π^* transition.[26]

The O 1s spectra (Figure 2, right) has a lower number of electronic transitions than the C 1s spectra. As is evident from the molecular structure shown in Figure 1, there are two types of oxygen sites: the carbonyl and the sulfonated oxygen. The lowest energy peak is attributed to O 1s(O=C) → $\pi^*_{O=C}$ (530.8 eV), and the second discrete transition involves the sulfonated oxygen, O 1s(SO_3) → $\pi^*_{O=S}$ (533.8 eV).[26] The higher energy peaks, at about 540 and 545 eV, can be attributed to O 1s(SO_3) → $\sigma^*_{(O-S)}$ and O 1s(O=C) → $\sigma^*_{(O-C)}$ transitions, respectively.[26]

Taking into account the C 1s transitions involved, three excitation energies were selected for the present study: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV).

MANTMS Homopolymer. XPS wide-scan spectra obtained from pristine thin films of MANTMS homopolymer and MANTMS−MMA copolymer show four main signals corresponding to S 2p−2s, C 1s, O 1s, and F 1s (Figure S2, Supporting Information). Irradiation of the films and exposure to oxygen showed different photodegradation processes, depending on the polymer type and excitation energy. Table S1 (Supporting Information) summarizes the corrected chemical composition calculated from the relative areas of the XPS spectra for the untreated and treated homopolymer and copolymer thin films. The dependence of the F 1s and S 2p XPS signals on the irradiation time is presented in Figure 3. The data in Figure 3 show a clear defluorination and loss of sulfonated groups with the increase in the irradiation time for the MANTMS homopolymer. The effect is particularly evident when the excitation energy corresponds to C 1s → $\pi^*_{C=C}$ and contrasts with excitations to $\pi^*_{C=O}$ and σ^*_{C-F} orbitals.

Untreated MANTMS homopolymer films showed typical signals corresponding to the aliphatic and aromatic contributions: (C−C/C−H), C−O, COO, and CF_3 functionalities (see Figure 4 top). After 1 min of irradiation at the C 1s → $\pi^*_{C=C}$ excitation (285.3 eV), the CF_3 and COO contributions in the HR-XPS spectrum almost disappeared. Additionally, the intensity of the C−O contribution was also affected by 285.3 eV. This strong effect of defluorination and loss of sulfonated groups under irradiation was also observed in our previous EUV studies of resists irradiated at 103.5 eV.[7,8] The signals of C 1s and O 1s also changed during irradiation, but due to the reorganization and oxidation processes, they did not show a clear tendency (Table S1, Supporting Information). On the contrary, the MANTMS−MMA copolymer resisted the irradiation with a lower rate of defluorination and loss of sulfonated groups for all the excitation energies studied (see Figure 3).

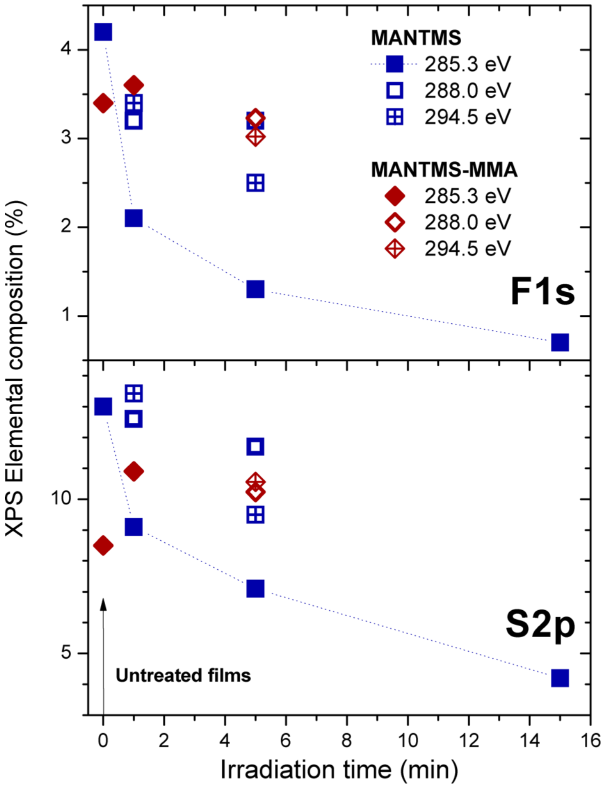


Figure 3. Fluorine and sulfur atomic percent concentration of untreated and irradiated films at specific inner-shell excitation energies measured by XPS. Excitation energies selected for irradiation: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV).

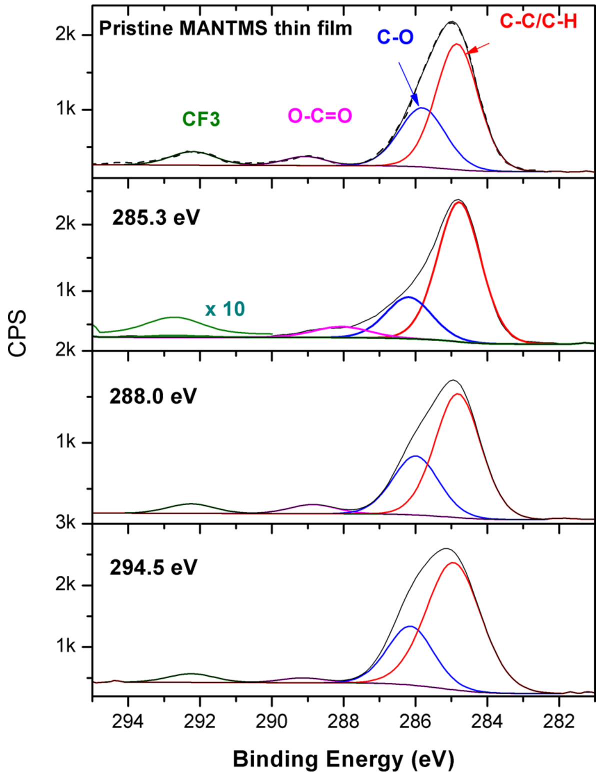


Figure 4. High-resolution XPS spectra of the C 1s envelope of the MANTMS homopolymer films before and after 1 min of irradiation via synchrotron radiation at several excitation energies corresponding to the following transitions: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV).

HR-XPS spectra clearly show that when the excitation energy was set to 288.0 eV (C 1s → $\pi^*_{C=O}$ transition) or 294.5 eV (C 1s → σ^*_{C-F} transition), the loss of fluorine and sulfur was much lower than at 285.3 eV (see Figure 4 and Table S1, Supporting Information). It is necessary to point out that the absolute number of photons reaching the samples was up to 20% higher at 288.0 and 294.5 eV than at 285.3 eV according to the absolute photon-flux curve of the SGM grating monochromator. In spite the fact that the dose at 288.0 and 294.5 eV was higher than at 285.3 eV, Figure 4 and Table 1 show that after the first minute of irradiation at excitation energies corresponding to C 1s → $\pi^*_{C=O}$ and C 1s → σ^*_{C-F} transitions, the HR-XPS spectra did not suffer significant changes. There is a decrease in the signal intensity of the CF_3 and COO functionalities after irradiation at 288.0 and 294.5 eV (see Table 1), but their binding energies remaining constant; i.e., the MANTMS homopolymer did not photodegrade to a significant extent. Those results contrasted with the irradiation of the polymer at 285.3 eV. Table 1 shows that after 1 min of excitation at 285.3 eV almost no CF_3 signal can be quantified, and the "COO" binding energy moved to lower energy (~288.0 eV). This shift in the binding energy means that a new functionality, C=O, has to be introduced in the fitting process (see Table 1). Table 1 also shows the quantification of F 1s and S 2p signals from the HR-XPS spectra. At 285.3 eV, the signal intensity of F 1s and S 2p decreased 50% and 30%, respectively, after 1 min of irradiation compared to the elemental concentration measured for an untreated film. At 288.0 and 294.5 eV, the decrease in signal intensity for F 1s and S 2p is much lower, and in particular, for S 2p there was almost no change after 1 min of irradiation at 294.5 eV. In conclusion, a clear effect on the bond-breaking selectivity at the C 1s → $\pi^*_{C=C}$ excitation can be noticed (see Table S1 of the Supporting Information for more details). In addition, the MANTMS homopolymer suffers an important scission in the ester group mainly at 285.3 eV of excitation energy, forming C=O functional groups previously nonexistent in the pristine resist and producing a strong defluorination effect and loss of sulfonated groups under irradiation.

In order to examine the effect of the irradiation at different excitation energies in more detail, NEXAFS spectra were acquired. Figure 5 shows the NEXAFS spectra of MANTMS homopolymer thin films after irradiation at the three excitation energies chosen in the present study at different irradiation times. Irradiation at 285.3 eV, where the electron is promoted from a carbon inner-shell 1s orbital to an antibonding $\pi^*_{C=C}$, led in 1 min to almost the disappearance of the double bond signal (see Figure 5). The surface changes produced after 1 min of irradiation were similar to that obtained after 5 or 15 min of irradiation, showing a very efficient process of dissociation and reorganization of the polymer structure after illumination at 285.3 eV (see Figure S3 in Supporting Information). NEXAFS spectroscopy is highly sensitive to surface chemical changes, and therefore, it shows drastic modifications in the surface chemistry of the polymer after irradiation and oxidation of the surface. The triflate group is affected and no signal of the C 1s transition, $C-SO_3$ → π^*, is seen in the spectrum after irradiation. In our previous study with nonresonance excitations, it was observed that the homopolymer easily lost the triflate functionality by breaking the labile F_3C-SO_3 bond

Table 1. High-Resolution XPS Peak-Fitted Components of the C 1s Spectra (from Figure 4) for Untreated and Irradiated MANTMS Homopolymer Thin Films at the Three Excitation Energies (EE) Chosen in the Present Study and the Decrease in F 1s and S 2p Signals Calculated from the XPS Survey Spectra for Irradiated Homopolymer Films

	functional group composition (%)					signal intensity decrease (%)[a]	
EE (eV)	CF_3	O−C=O	C=O	C−O	C−C/C−H	F 1S	S 2p
untreated	6.8	4.2		30	59		
285.3	∼0	5.5	12.7	25.4	56.4	50	30
288.0	4.6	4.5		29.3	61.6	23.8	3
294.5	3.8	2.1		26.1	68	19	∼0

[a] Decrease in the intensity signal (%) calculated from XPS survey spectra after 1 min of irradiation compared with the pristine polymer (for more details see Table S1 in the Supporting Information).

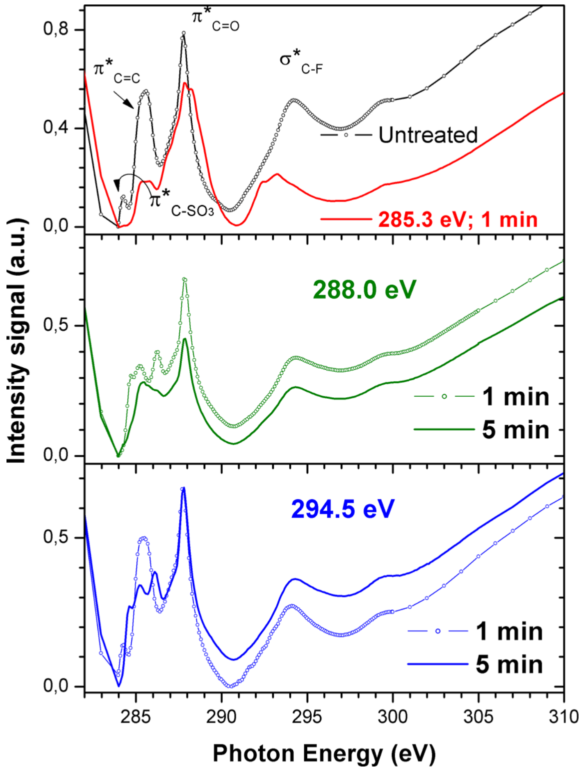


Figure 5. Carbon K-edge NEXAFS spectra of untreated and SR-irradiated MANTMS homopolymer thin films for 1 and 5 min irradiation time. Excitation energies marked with arrows corresponding to the following transitions: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV).

after irradiation. A fast desorption of SO_2^+, SO^+, and CF_3^+ fragments (m/z = 64, 48, and 69, respectively) was measured by a quadrupole mass spectrometer integrated into the vacuum chamber.[8] Therefore, a loss of the C−SO_3 → π* signal after irradiation and the subsequent fast energy transfer process should be expected. Additionally, the transition to the $\pi^*_{C=O}$ orbital is wider than the pristine polymer signal, and there is also a shift in the maximum of the peak. These changes reflect important modifications in the chemical environment around the ester groups when compared to the untreated polymer.

The shoulder at the lower energy of the $\pi^*_{C=O}$ transition (see Figure 5), which appeared after irradiation at ∼286.8 eV, can be assigned to the σ^*_{C-H} transition[27] or carbonyl groups that have a transition energy of about 287 eV.[28] Additionally, the C $1s_{(C=O)}$ → $\pi^*_{(C=O)}$ transition, originally at 287.8 eV, shifted 0.4 eV at higher energies, showing a more electronegative environment around the original ester groups.[29] Similar shifts in energy of the $\pi^*_{C=O}$ peaks are typically found in urea and urethane compounds, where the $\pi^*_{C=O}$ peak in urea is 0.5 eV lower in energy than the $\pi^*_{C=O}$ peak in urethanes.[29] All those changes may reflect the high reactivity of the benzyl rings after irradiation and oxidation. Finally, the transition to σ^*_{C-F} (294.5 eV) almost disappeared and the spectra may show original and new σ^*_{C-C} transitions. These last results agree with the XPS data (see Figure 4), where there is a strong decrease in the CF_3 and COO functionalities at 285.3 eV of excitation energy.

Excitation to $\pi^*_{C=O}$ and σ^*_{C-F} shows a different picture (see Figure 5, middle and bottom panels). First, the transition to σ^*_{C-F} (294.5 eV) had no significant change after irradiation, even after 5 min of continuous SR light reaching the substrate. Direct excitation to $\pi^*_{C=O}$ decreased the intensity of the C 1s → $\pi^*_{C=O}$, but even after 5 min of irradiation, the peak position and width of the peak at 287.8 eV did not change, showing that the COO functionalities present on the surface correspond mainly to the pristine polymer. Excitations at 288.0 and 294.5 eV affected the carbon−carbon double bonds with a much lower level of modifications than direct $\pi^*_{C=C}$ excitation (compare with Figure 5, top). At an excitation energy of 294.5 eV, the carbonyl signal is preserved, and the $\pi^*_{C=C}$ is only affected after 5 min of irradiation. These results show that direct excitation of transitions involving carbonyl and C−F groups did not affect the triflate group significantly.

The analysis of the O 1s NEXAFS results after irradiation illustrates the photofragmentation dependence on the excitation energy. Actually, oxygen inner-shell excitation spectra showed clearer evidence about the selectivity of the excitation than the C 1s NEXAFS results. Figure 6 presents the results obtained for the O 1s energy region after the normalization process.[30] The presence of oxygen in the SGM line introduced a constant "dip" in the O 1s spectra, and for this reason, a final normalization of the dips at about 534.4 eV was carried out. As can be seen in Figure 6, excitation at 285.3 eV strongly changed the shape and peak position of the spectrum, suggesting a drastic modification of the surface chemical composition after 1 min of irradiation at the energy corresponding to the C 1s → $\pi^*_{C=C}$ excitation. Figure 6 shows a shift to higher energies of about 0.3−0.4 eV in the O 1s(O=C) → $\pi^*_{O=C}$ transition and a strong decrease in the sulfonated oxygen signal [O 1s(SO_3) → $\pi^*_{O=S}$]. The above shift in the $\pi^*_{O=C}$ transition is very close to the same excitations measured by Ishii et al. for propiolic and acrylic (531.5 eV) acids.[28] In the case of propanoic acid, the same authors observed an O 1s(O=C) → $\pi^*_{O=C}$ transition at a higher energy of 532.1 eV. Therefore, in our study it can be assumed that there was a dissociation of a double bond in the naphthyl functional groups after excitation followed by oxidation of the radicals formed when oxygen was

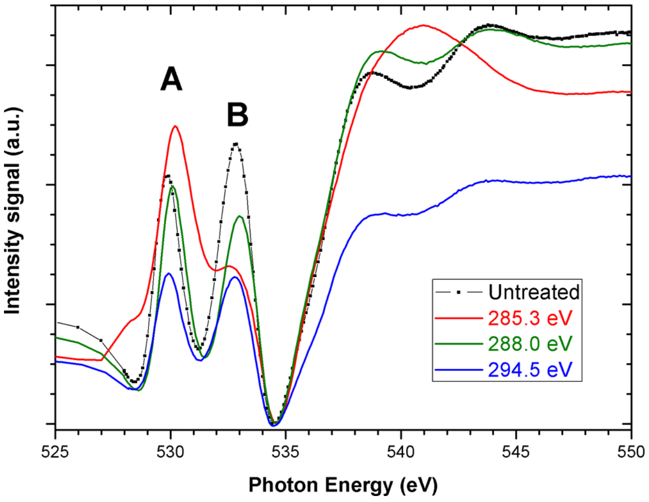


Figure 6. Oxygen K-edge NEXAFS spectra of untreated and SR-irradiated MANTMS homopolymer thin films. Irradiation time: 1 min. Excitation energies corresponding to the following transitions: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV). For the A and B ratio, see Table 2 and the text.

introduced into the UHV chamber. It is already known that in an inert atmosphere, such as a vacuum or an unreactive gas, X-ray-generated radicals are more stable. In an atmosphere containing oxygen, the radicals can react to form peroxides or hydroperoxides, accelerating the rate of radiation degradation or the extent of the radiation damage.[31] A new signal at a lower energy of approximately 529.5 eV shows a less electronegative environment around the excited oxygen atom. The origin of this signal is uncertain, because it could be assigned to the aldehyde or ketone functional groups, but the energy of these groups would be very close or slightly higher than 531.0 eV, depending on the compound.[32] An artifact due to the normalization process cannot be ruled out.

Table 2 shows the changes in the A/B signal ratio, measured from the maximum peak height, with the increase in photolysis time and its dependence on the excitation energy. Only 1 min of irradiation at 285.3 eV led to an increase of about 120% in the A/B ratio from ∼0.9 to ∼1.9. When the irradiation was set to 288.0 or 294.5 eV, a maximum increase in the A/B ratio of ∼44% or ∼11%, respectively, for an irradiation time of 5 min was observed (see Table 2). Clearly, these results confirm the highly selective photofragmentation process that occurs after the C 1s → $\pi^*_{C=C}$ excitation that produced a highly efficient dissociation of a double bond in the naphthyl functional groups.

Table 2. Effect of Selective Excitation Energy and Irradiation Time in MANTMS Homopolymer Thin Films on the NEXAFS O K-Edge Ratio Signal A/B (see Figure 6)

		NEXAFS O K-edge ratio A/B[a]	
EE (eV)	irradiation time (min)	MANTMS homopolymer	MANTMS−MMA copolymer
untreated		0.9	1.57
285.3	1	1.9	1.6
	5	2.2	2.6
288.0	1	1.15	
	5	1.3	1.5
294.5	1	1.0	
	5	1.0	1.5

[a] A = O 1s(O=C) → $\pi^*_{O=C}$ and B = O 1s(SO_3) → $\pi^*_{O=S}$.

The high-energy peaks attributed to O 1s(SO_3) → $\sigma^*_{(O-S)}$ and O 1s(O=C) → $\sigma^*_{(O-C)}$ transitions were also strongly affected, and a new signal probably corresponding to a typical O 1s → $\sigma^*_{(O=C)}$ transition appeared in the spectra. All these results confirmed the loss of sulfonated groups after irradiation. The surface changes produced after 1 min of irradiation at 285.3 eV were enough to completely modify the chemical surface composition. Irradiation of the polymer for longer times (5 and 15 min) produced similar O 1s spectra to 1 min irradiation with lower intensity (see Figure S4 in the Supporting Information). On the contrary, excitations at 288.0 and 294.5 eV (see Figure 6) showed that the oxidized polymer sections kept their carbonyl functionalities after irradiation. Excitations to $\pi^*_{C=O}$ (288.0 eV) and σ^*_{C-F} (294.5 eV) orbitals almost preserved the original chemical structure in relation to oxygenated functional groups. These results agree with what the carbon inner-shell results showed before.

MANTMS−MMA Copolymer. At a first glance, Figure 3 shows that the MANTMS−MMA copolymer is more resistant to the SR irradiation. While MANTMS homopolymer thin films suffer a continuous defluorination and loss of sulfonated groups with the increase in the irradiation time, the MANTMS−MMA copolymer shows a much lower degree of photodegradation. The effect is evident with the labile S 2p components, where the XPS signal was almost constant after 5 min of irradiation (see Figure 3, bottom).

Carbon inner-shell NEXAFS spectra show the higher stability of the MANTMS−MMA copolymer thin films in Figure 7. Excitation at 285.3 eV produced a strong decrease in the transition, corresponding to the C 1s → $\pi^*_{C=C}$, but the C 1s → $\pi^*_{C=O}$ and C 1s → σ^*_{C-F} signals did not noticeably change compared with the changes observed during the irradiation of MANTMS homopolymer films at the same excitation energy (see Figure 5, top). The irradiation resistance of the copolymer is evident at excitation energies C 1s → $\pi^*_{C=O}$ and C 1s → σ^*_{C-F} (see Figure 7, middle and bottom). In our previous work, it was hypothesized that the copolymer may develop a rearrangement during irradiation that finally kept the S−C and SO_x functional groups almost intact.[7] We have also observed that in copolymers of MMA and poly(MAPDST-*co*-MMA), the former acts as a dissolution inhibitor, whereby patterning can be achieved at lower doses versus the MAPDST homopolymer. From this, we can infer that the MMA unit in the polymer microstructure provides photostability. In effect, it can be concluded that the MMA is more stable toward EUV radiation compared to the sulfonyl moieties.

To confirm the higher stability against radiation damage of the MANTMS−MMA copolymer films, O 1s NEXAFS spectra were obtained and compared to those of a pristine film. The results are shown in Figure 8. Irradiation at 285.3 eV mainly decreased the sulfonated oxygen signal at lower energies [O 1s(SO_3) → $\pi^*_{O=S}$], similar to what was observed for the MANTMS homopolymer, but for the copolymer films, 5 min of irradiation was necessary to observe an approximate 65% increase in the A/B ratio (see Table 2). The longer irradiation times were also necessary to see a modification of the higher energy signals [see O 1s(SO_3) → $\sigma^*_{(O-S)}$ and O 1s(O=C) → $\sigma^*_{(O-C)}$ transitions in Figure 8]. This result contrasted with the irradiation of the homopolymer, where in only 1 min of illumination a drastic change was observed in the oxidized

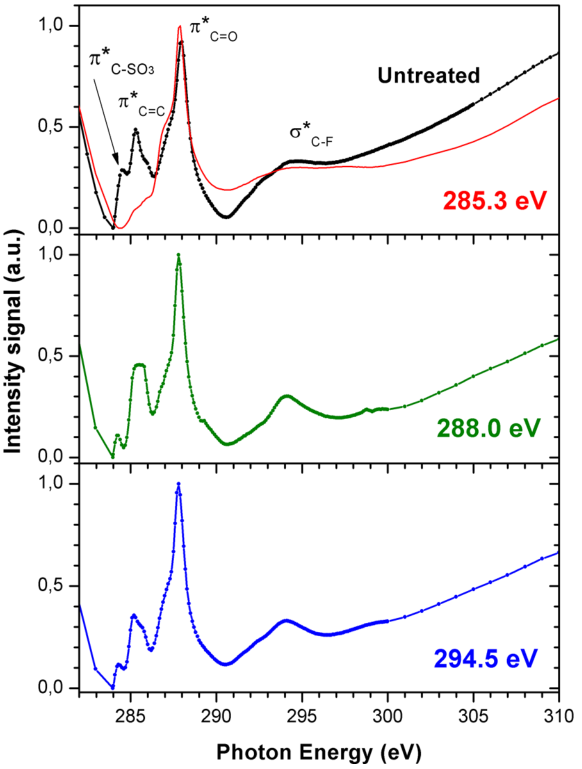


Figure 7. Carbon K-edge NEXAFS spectra of untreated and SR-irradiated MANTMS−MMA copolymer thin films at several excitation energies corresponding to the following transitions: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV). Irradiation time: 5 min.

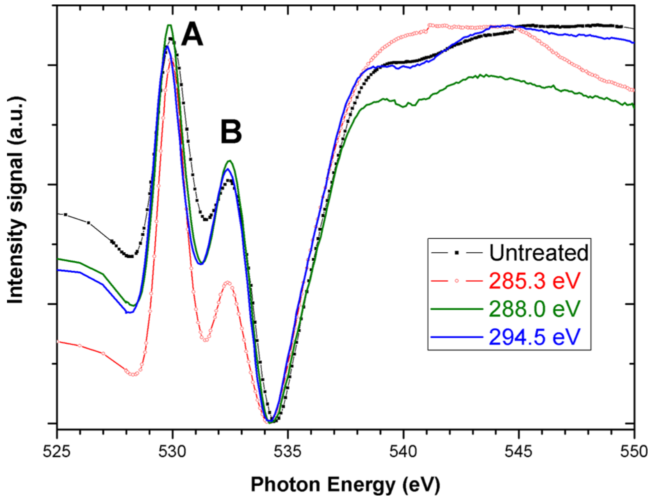


Figure 8. Oxygen K-edge NEXAFS spectra of untreated and SR-irradiated MANTMS−MMA copolymer thin films at excitation energies corresponding to the following transitions: C 1s → $\pi^*_{C=C}$ (285.3 eV), C 1s → $\pi^*_{C=O}$ (288.0 eV), and C 1s → σ^*_{C-F} (294.5 eV). Irradiation time: 5 min.

surface compared to a pristine film (see Figure 6 and Table 2). When the energy was tuned to C 1s → $\pi^*_{C=O}$ and C 1s → σ^*_{C-F}, no significant changes in the spectra were observed (see Figure 8 and Table 2). It is necessary to point out that the irradiation time in Figure 8 was 5 min, and even with this high illumination time of SR, the copolymer could dissipate the excitation energy very efficiently without appreciable photodegradation.

CONCLUSIONS

We presented two different kinds of organic polymeric resist materials that contain photosensitive tetrahydrothiophenium and trifluoromethanesulfonate groups and various energy-absorbing moieties to improve the sensitivity toward radiation. Irradiation at selected carbon inner-shell excitations shows a selective photodegradation process. Tuning the excitation energy to C 1s → $\pi^*_{C=C}$ easily dissociated the C═C double bond in the naphthyl functional groups, leading to the formation of new ester groups after oxidation and simultaneous loss of C−F and SO_x functionalities. The defluorination and loss of sulfonated groups with the increase in the irradiation time for the MANTMS homopolymer was evident when the excitation energy was tuned to excite the $\pi^*_{C=C}$ transition. On the contrary, C 1s → $\pi^*_{C=O}$ and C 1s → σ^*_{C-F} excitations did not produce important changes in the polymer surface region, in spite of the fact that the photon flux at these excitation energies was about 20% higher than for a C 1s → $\pi^*_{C=C}$ excitation. When the excitation energies corresponded to $\pi^*_{C=O}$ and σ^*_{C-F} excitations, the original chemical structures of the polymers seemed to be efficiently preserved. Irradiation of the MANTMS−MMA copolymer films showed an even higher stability of the copolymer against radiation damage. The presence of the methyl methacrylate copolymer helped to dissipate the excitation energy much more efficiently, avoiding significant photodegradation of the polymer. The results presented highlight the importance of selecting the right functional groups (polymer formulation) and excitation energy to produce an efficient functionalization of a polymer film for EUVL.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization of radiation-sensitive organic polymers (MANTMS homopolymer and MANTMS−MMA copolymer) together with additional information on XPS and NEXAFS results. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03378.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partially supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), (processes no. 550461/2012-4 and 477200/2012-5) and LNLS-National Synchrotron Light Laboratory, Brazil. The authors would also like to deeply acknowledge the technical assistance of the Accelerator Group, especially the VUV and Soft X-ray Spectroscopy Group. The authors G.C. and G.K.B. acknowledge receipt of CAPES fellowships for financial support. K.E.G. acknowledges partial support from Intel Corp. USA. Discussions with Dr. Subrata Ghosh (IIT Mandi) are also acknowledged with regard to the synthesis of the polymers.

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