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# Mechanistic Insights of Sn-Based Non-Chemically-

# **Amplified Resists under EUV Irradiation**

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### ABSTRACT

Formulating high sensitivity and resolution in Extreme Ultraviolet (EUV) resists is a serious concern regarding the adaptation of EUV lithography. The incorporation of a high optical density Sn compound MAPDST-co-ADSM (4-(methacryloyloxy)phenyl) in dimethylsulfoniumtrifluoromethane sulfonate-co-(acetyldibutylstannyl methacrylate), a non-CAR photoresist, exhibits lithography resolution for sub-15 nm node when patterned under e-beam and Helium ion irradiation. The synthesized resists were irradiated at 103.5 eV (~ 92 eV) using monochromatic synchrotron radiation. After EUV irradiation and oxidation, the resists were investigated using XPS, NEXAFS and by theoretical calculations (FEFF9 modeling program). It was observed significant changes in the labile CF3SO3- moiety, but interestingly its total dissociation or desorption was not observed after long exposure times. Bonds rearrangements of, formation of SnO2 and new SDC/C-F functionalities after irradiation were detected. Those complex processes suggested the existence of important sinks for the high photon energy absorbed, which in turn increased the lithography resolution. The present results highlight the importance of the incorporation of a heavy metal covalently linked to the main polymer structure. The enhanced resolution observed in the MAPDST-co-ADSM resist formulation using standard processing conditions, establishes its potential candidature as a EUVL resist for rapid prototyping of semiconductor devices.

### **1. INTRODUCTION**

From the beginning the semiconductor industry has realized that changes in optics components, sources with shorter excitation wavelengths, masks and photoresists needed to evolve to allow the continuous decrease in the critical dimensions of the node technology process [1]. From nearly four decades, silicon wafers coated with photoresists have been exposed to selective radiation to induce chemical changes, which in turn modify the solubility of the resist material after exposure and post bake. In spite of the efforts carried out in the last decade to introduce extreme ultraviolet (EUV) radiation in the lithography process (EUVL) there is still a significant concern about the anticipated switching to EUVL [2]. The actual main challenges are to find a suitable resist for EUVL and to understand the complexity of the EUV processes involved.

EUV photons of  $\lambda$ =13.5 nm have much higher energy (92 eV) than those used in UV and Deep-UV photolithography. The absorption of the EUV photons is not resonant, which means that the absorption cross section ( $\sigma$ ) are very low for typical resists containing light elements, but simultaneously EUV is an ionizing radiation. EUV photons produce a high yield of secondary electrons inducing different and complex chemistry because the energy of the ejected electrons is usually higher than the binding energies. The emitted electrons can start a series of secondary processes such as electron attachment, internal excitation and ionizations leading finally to bond dissociations and polymer rearrangements.

The need to increase the  $\sigma_{EUV}$  has led to several research groups, including our self, to synthesize new polymer resists containing a heavy metal centre absorber moiety. A series of works were published on EUV irradiation of resists containing heavy metals and its oxides, such as Sb [3-7], Sn [8-12], Pt and Pd [13], Hf [14-17], Ti [18, 19], Zr [14, 20], Co,

Fe and Cr [21] and even containing a light atom such as Al [22]. Simultaneously as the pattering is approaching to the molecular/atomic level, the community also started to focus the research in the understanding of the fundamental phenomena of the interaction of EUV photons with the polymers thin films. In this sense, Monte Carlo simulations [23], analytical models [23], stochastic models [24], the percolation theory [25] and a combination of density functional theory, molecular dynamics and the finite difference method [26] have been used recently to simulate the interaction of EUV photons with the resist materials.

Within all the heavy metals studied Sn, in particular, has been investigated in recent times in more detail. Organotin compounds fulfill the very high  $\sigma_{EUV}$  property needed and their compounds may have the ability to enable higher resolution patterning. For instance, Cardineau et al. have suggested that the strength of the C-Sn bond and dissociation mechanisms can be correlated to the EUV photosensitivity (minimum dose used in mJ/cm<sup>2</sup>). The sensitivity of Sb-oxide films to EUV light was investigated as a function of structural changes of the counter-anions (carboxylates) and organic ligands that were bounded to Sb [11]. Temperature-programmed desorption, electron stimulated desorption and X-ray photoelectron spectroscopy (XPS) techniques were used to understand the behavior of organotin photoresists under EUV exposure [12]. It was shown a relative high desorption of butyl groups under irradiation highlighting the importance of the presence of low energy electrons in the EUV patterning process. Ambient-Pressure XPS was mainly used to investigate the reaction mechanisms that govern the solubility transitions in organotin-based photoresists [10]. Their main results showed the cleavage of the Sn–C bonds and desorption of butyl ligands from the Sn clusters after EUV irradiation. Significantly, a higher rate for butyl group desorption was measured when oxygen was present during irradiation suggesting that new reactive oxygen species can react with two Sn groups in adjacent

clusters leading to Sn–O–Sn linking. In a recent work, Enomoto *et al.* introduced an organotin compound in a n-CAR resist and found an increase of more than 2.5 times in sensitivity suggesting that the sensitivity enhancement was due to the generation of polymer radicals through the Sn–C bond scission [9]. Finally, Fredericka *et al.* in an interesting work have studied thin films of a butyltin oxide hydroxide (BuSnOOH) as an organotin molecular resist model [8]. Their main results showed that exposure to radiation formed insoluble films. It was suggested that the loss of butyl groups and the increase in the oxygen-tin network appear to be important factors for the observed solubility change.

In this study we present the EUV results of a new Sn-based hybrid n-CAR resist, MAPDST-*co*-ADSM (where MAPDST = (4-(methacryloyloxy)phenyl) dimethylsulfonium trifluoromethanesulfonate and ADSM = (acetyldibutylstannyl methacrylate)) synthesized through free radical polymerization process. We have studied in the past the EUVL performance and the fragmentation process after EUV irradiation of several n-CAR resists [27-29] including in some cases a heavy metal (Sb) in the resist structure [7]. The recent interest in the study of EUV irradiation of organotin compounds involves necessarily the understanding of the photofragmentation processes under EUV irradiation, which in turn will guide the synthesis of new EUVL resists. Here, the EUV photofragmentation process MAPDST-*co*-ADSM resists was investigated using XPS and Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy techniques. Additionally, theoretical calculations carried out using the FEFF9 modeling program allowed to confirm the Sulfur *L*-edge assignments and suggested the new functionalities observed experimentally.

### **2. EXPERIMENTAL SECTION**

### 2.1. Materials.

High purity Nitrogen (99.999%) and Oxygen (99.999%) gases were purchased from White Martins-Praxair, Inc. and used as received. All the chemicals used during synthesis and processing were purchased from Merck (Sigma Aldrich).

### 2.2. Synthesis and characterization of MAPDST-co-ADSM photoresist

The MAPDST-co-ADSM (95:5 feed ratio) co-polymer was synthesized by the reaction between radiation sensitive organic monomer MAPDST (95% feed ratio) and inorganic monomer ADSM (5% feed ratio) in ACN/THF (1:2) solvent system using AIBN (1wt% relative to both monomers) as a free radical initiator under nitrogen atmosphere at 60°C for 2 days. The synthetic route for MAPDST-co-ADSM copolymer is given in Scheme 1. The synthesized resist was wellcharacterized using NMR, GPC, TGA, FTIR and EDX spectroscopic techniques (see Fig. S1-S7 in the SI). The calculated molecular weight (Mw) and poly-dispersity index (PDI) of the MAPDST*co*-ADSM copolymer was calculated from the GPC analysis as 8221 g/mol and 1.51 respectively (see, Fig. S4 in the SI). EDX analysis on MAPDST-co-ADSM resist thin films reveal the presence of C, O, F, S and Sn elements, which conclude that the presence of Sn and MAPDST monomers in the resist structure (Figure S5). The percentage of Sn (2.03) in the copolymer MAPDST-co-ADSM (95:5 feed ratio) was estimated from a master calibration (see, Fig. S15) based on ICP-OES analysis of multiple analogous samples reported recently [31]. The copolymer composition based on this estimation was determined to be as shown in scheme 1, wherein 1 and m values are 94% and 6%respectively. The thermo gravimetric analysis (TGA) reveals that the compound was stable up to 190 °C and started decomposition after 220 °C, this study indicates that MAPDST-co-ADSM resist having suitable thermal stability for lithography studies especially during pre and post-exposure baking (see, Fig. S6 in the SI).



Scheme 1: Synthesis of MAPDST-co-ADSM copolymer.

Synthetic procedure of hybrid resist, MAPDST-*co*-ADSM formulation employed was as follows: the radiation sensitive organic monomer MAPDST (1g, 2.680 mmol), hybrid Sn-based monomer ADSM (0.051 g, 0.134 mmol) and azobisisobutyronitrile (AIBN) (1 weight %, relative to both monomers) were taken in a schlenk flask under N<sub>2</sub> atmosphere in darkness. To this, 15 ml dry solvent THF–CH<sub>3</sub>CN (2:1) was added to the reaction mixture under nitrogen atmosphere. Thereafter, the reaction mixture was transferred into a clean oven dried polymerization flask with side arm neck via filtering the reaction mixture through 0.4  $\mu$ m Teflon filters. In order to remove oxygen in the reaction mixture, several rounds of freeze-thaw cycles (6-7 cycles) were conducted with N<sub>2</sub> purging. Thereafter, reaction mixture was poured slowly into diethyl ether (50 mL) and the separated solid was washed several times with diethyl ether. The resulting crude product was dissolved in methanol and then re-precipitated using diethyl ether. Finally, the separated white product was filtered-off and dried in a temperature controlled hot air oven at 50 °C for 1 day. Yield: 490 mg (49.1%); FT-IR: vmax/cm<sup>-1</sup> 3022-2859 (CH), 1748 (C=O), 1586-1493 (C=C), 1248 (CF<sub>3</sub>),

1095-1026 (C-O), 515 (Sn-C);<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta_{\rm H}$  8.02 (2H, br peak, m,m'-ArH), 7.46 (2H, br peak, o,o'-ArH), 3.25(6H, s, S(CH<sub>3</sub>)<sub>2</sub>), 3.18 (3H, s, CH<sub>3</sub> acetate), 2.4-1.0 (5H, br m peak, CH<sub>2</sub> and CH<sub>3</sub> polymeric&aliphatic protons); <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>)  $\delta_{\rm C}$  174.2 (C=O, acetate), 162.3(C=O), 153.6, 132.2, 131.8, 131.6, 124.4, 123.9, 123.1, 121.9, 119.3, 117.2, 116.8, 114.0 (aromatic, CF<sub>3</sub>), 45.3 (O-CH<sub>3</sub>), 28.8 (S-CH<sub>3</sub>), 28.3; <sup>19</sup>F NMR (376 MHz; DMSO-d<sub>6</sub>)  $\delta_{\rm F}$ -77.6 (3F, s, CF<sub>3</sub>).

### 2.3. EUV irradiation study

The photofragmentation study of the MAPDST-co-ADSM thin films was performed according to the methodology used in our previous works [7, 28]. Briefly, irradiation of the resist thin films was carried out for a fixed period of time inside the UHV chamber ( $P \sim 1 \times$ 10<sup>-9</sup> mbar). After irradiation, the samples were transferred to the UHV preparation chamber and pure oxygen at a pressure of about 10<sup>-5</sup> mbar was introduced for 30 min. After oxygen exposure, the samples were moved back to the UHV chamber for further analysis. The synchrotron radiation (SR) light was delivered from the PGM beam line for EUV, VUV, and soft x-ray spectroscopy of the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil using a planar grating monochromator to select photons in the range of 100–1500 eV. The resolving power ( $\Delta E/E$ ) of the PGM beamline was between 1,000 and 25,000. The EUV photon fluxes at the sample positions were typically between 10<sup>11</sup> and 10<sup>13</sup> photon/s and the spot size of the photon beam at the sample was  $\sim 500 \,\mu\text{m}$ . The photon flux at 103.5 eV was about 4 x  $10^{12}$  photon s<sup>-1</sup> or ~5 x  $10^{13}$  photon s<sup>-1</sup> cm<sup>-2</sup>, a few hundred times higher than the regions used for the acquisition of the NEXAFS and XPS spectra. No charging effects in the XPS and NEXAFS spectra were observed and beam damage in the analysis can be ruled out. For example, after 10 min of continuous irradiation the maxima correction observed for a typical C 1s XPS spectra was 2 eV. Light from 12 nm (103.5 eV) was chosen

for the EUV investigation instead of 13.5 nm (92 eV) due to its high undulator intensity and it was very close to the light energy established for resist patterning 13.5 nm. The Si wafers substrates were directly attached to the sample holder using conducting double-sided tape. A computer-controlled XYZ sample manipulator housed in the UHV analyses chamber allowed sub-millimetric precision. The treated film areas were confirmed by moving ~1 mm up-down or right-left the XYZ sample manipulator where the acquired NEXAFS and XPS spectra were identical to the untreated films.

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 using this flux spectrum to correct for fluctuations in beam intensity. NEXAFS data were analyzed following the standard procedures where all spectra were processed using a constant-value pre-edge subtraction and post-edge normalization [30]. The final analysis of NEXAFS data including peak fitting was performed using the software package ATHENA [31]. Absolute photon energy calibration was carried out by the photoemission signal of the Au  $4f_{7/2}$  and then plotting the second derivative of the C 1s  $\rightarrow \pi^*_{C=C}$  signal. The calibration value of 285.3 eV was introduced.

XPS spectra were recorded using a high-performance hemispheric SPECSLAB II energy analyzer (Phoibos-Hs 3500 150 analyzer, SPECS, Berlin, Germany) and the binding energy calibration was made using Au 4f<sub>7/2</sub> (83.96 eV). In general, all survey spectra and F 1s, O 1s, Sn 3d and the high resolution (HR)-XPS spectra were acquired using a photon energy fixed at 728 eV. When depth chemical information was probed, the excitation energy was changed to 940 eV or 1026 eV. In the cases of recording the HR-XPS of C 1s and S 2p the excitation energy was set at 368 eV. A pass energy of 30 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. Data were analyzed using the CASAXPS (Version 2.2.87 software). The HR- XPS envelopes were analyzed and peak-fitted after subtraction of the Shirley background using Gaussian–Lorentzian peak shapes.

### 2.4. Computational Methods

The Gaussian09 program [32] was used for the conformational search of the monomer. The obtained conformers were refined with complete geometry optimization within the B3LYP functional. The SDD (Stuttgart/Dresden) effective corepotential [33, 34] was employed for Sn and the double- $\zeta$ quality plus polarization 6-31+G(d) basis set for all other elements [35]. The characterization of stationary points was done by Hessian matrix calculations and the energies used to compare the stability differences of the evaluated conformations included zero-point corrections. In order to simplify the conformational space of the monomer, and following theoretical studies of R-Sn(Bu)<sub>3</sub> compounds, the *n*-butyl groups were replaced by methyl [36].

For the optimization of the monomer model, an incremental approach was carried out. Initially, a conformational search of the structure of the cation was performed and 15 different geometries were evaluated (see Table S1 in SI). Then four groups of geometries were obtained after energy and RMSD comparison and for each group a particular geometry was selected for the anion inclusion. In order to do this, the different monomers were aligned with the structure found for a similar monomer model (poly(4-(methacryloyloxy) phenyldimethylsulfoniumtriflate) [27] and the coordinates of the anion were added to the new neutral models. After this final optimization the most stable structure obtained was employed for further studies (see Table S2 in SI). The XYZ coordinates and the final energies of the neutral monomer models are included at the end of the SI section.

Finally, the computer software program FEFF9 [37, 38] was employed for the theoretical simulation of the NEXAFS spectra. In a previous study the use of self-consistent spherical muffin-tin potentials and real space full multiple-scattering formalism confirmed the origin of the main resonances experimentally observed [27]. In the present work the FEFF9 formalism was used to compute the sulfur *L*-edge absorption spectra. With the atomic species and coordinates optimized by Gaussian09 within a cluster and no adjustable physical parameters, FEFF9 calculated the scattering contributions to the sulfur *L*-edge absorption spectra to all orders within the cluster. The resolving spectral resonances are solved by projecting the full scattering matrix onto the direction of a polarization vector calculating any theoretical orientation dependence of the NEXAFS spectrum.

## **3. RESULTS AND DISCUSSION**

### 3.1. X-ray photoelectron spectroscopy.

XPS was used to analyze the film composition and chemical changes that occur after radiation exposure at 103.5 eV of the MAPDST-*co*-ADSM films. Fig. 1 shows the relative elemental composition modifications obtained from the corresponding survey spectra of the films as a function of the irradiation time. This general picture of chemical surface changes show, at a first glance, that with the increase in irradiation time at 103.5 eV, there is an important relative decrease of O 1s signal, a partial decrease in F 1s and Sn 3d relative signals and an apparent relative increase in the S 2p signal. The results obtained were a bit surprising compared with our previous works of resist containing the triflate moiety. For instance, when MAPDST homopolymer thin films have been irradiated at 103.5 eV an

efficient loss of the triflate moiety was observed in less than 2 min with the concomitant merging of the corresponding positive  $SO_2^+$ ,  $SO^+$  and  $CF_3^+$  fragments measured by quadrupole mass spectrometry [39]. Similar behavior under 103.5 eV irradiation was previously observed when other resists containing the  $CF_3SO_3^-$  moiety were irradiated at 103.5 eV [7, 28, 29, 40]. We have also already shown that EUV irradiation of potassium trifluoromethanesulfonate thin films spin-coated on Si(100) led to a strong decrease in the typical signal features of the NEXAFS intensities [7]. Those data have evidenced the high sensitivity of the triflate functional group to EUV photons. The data presented in Fig. 1 may indicate that a different photofragmentation process can be present under EUV irradiation of the MAPDST-*co*-ADSM films.



**Fig. 1.** Dependence of the elemental relative atomic concentrations of untreated and irradiated MAPDST*co*-ADSM resist films on the irradiation time. Irradiation energy: 103.5 eV. Data obtained from survey XPS spectra with excitation energy of 728 eV. After irradiation, the samples were exposure to pure oxygen and then analyzed. Relative concentrations of the Sn 3d and F 1s are multiplied by the indicated values.

Trying to investigate in more detail the differences showed above with our previous works, the excitation energy for the XPS spectra was increased to 940 eV and 1026 eV. By this way chemical information goes beyond the surface region and probes deeper bulk

electronic properties of the films [41]. The results for 300 s of irradiation time at 103.5 eV are summarized in Table 1 and Fig. S8 (SI). The photoelectrons with the highest kinetic energies correspond to C 1s and S 2p. For example, at 728 eV their kinetic energies are about 443 eV and 564 eV respectively. At the same excitation energy of 728 eV the kinetic energy of the C 1s photoelectron is approximately 1.8, 2.3 and 11 times higher than Sn 3d<sub>5/2</sub>, O 1s, and F 1s respectively. It is expected that C 1s and S 2p signals represent chemical composition changes from deeper regions of the film. Therefore, the signals of the Sn 3d<sub>5/2</sub>, O 1s and particularly F 1s represent mainly surface changes.

**Table 1.** Elemental relative atomic percent concentrations of untreated and irradiated MAPDST-*co*-ADSM resist films as a function of the XPS excitation energy. Irradiation energy: 103.5 eV. Irradiation time: 300 s. After irradiation, the samples were exposed to pure oxygen and then analyzed.

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Excitation Energy (eV)	C 1s	O 1s	S 2p	Sn 3d	F 1s
728 (Pristine film)	72.5	12	12.5	0.8	2.2
728	80.3	5.9	12.6	0.5	0.7
940	80.3	8.6	9.4	0.7	1.0
1026	77.0	10.2	10.8	0.6	1.4

Girard-Lauriault *et al.* have developed a methodology based on the acquisition of XPS spectra at constant kinetic energies by tuning the synchrotron X-radiation energy [41, 42]. By this method, a constant and tunable information depth for all elements in a very thin organic layer can be obtained if a proper calibration procedure is done. In the present study, we did not carry out the specific calibration procedure suggested by the authors for the determination of the new relative sensitivity factors. Nevertheless, interesting information can be obtained when the XPS spectra of several atoms are compared at nearly constant

kinetic energies, i.e., the information depth is nearly constant for all the elements. The main data are summarized in the Fig. 2. All the photoelectrons have a kinetic energy variation of less than  $\pm 20\%$  (440  $\pm 80$  eV). The ratio of the kinetic energy of the C 1s photoelectrons to the kinetic energy of O 1s, S 2p, Sn 3d<sub>5/2</sub>, and F 1s photoelectrons is approximately 1.1, 0.8, 1.0 and 1.3 respectively. The irradiation of the films with 103.5 eV during 300 s showed that the fluorine atoms remained in the surface region after continuous irradiation (the F 1s relative concentration decreased about 50%) and surprising the signal of S 2p did not change at all (see Fig. 2). The Sn 3d relative concentration remained approximately constant and there was a decrease in the O 1s signal, in spite after irradiation, the samples were exposed to oxygen atmosphere. After 300 s of continuous irradiation of the MAPDST-co-ADSM resist films at 103.5 eV, Fig. 2 confirmed that the triflate moiety resisted the irradiation efficiently because the S 2p and in lower extend the F 1 s signals were detected in the surface region after that long irradiation period. Finally, it is possible to conclude that the minimum in relative concentrations observed in the Fig. 1 for the O 1s, Sn 3d and F 1s is due to the lower kinetic energy of the photoelectrons compared to C 1s and S 2p. For example, F 1s photoelectrons will have only 40 eV of kinetic energy at 728 eV of excitation energy. Those photoelectrons will be highly surface sensitive. On the contrary, the photoelectrons of C 1s and S 2p will have more than 10 times higher kinetic energies than the F 1s and therefore will show chemical information from the surface and deeper regions.



**Fig. 2.** XPS elemental composition of untreated and irradiated MAPDST-*co*-ADSM resist films at 103.5 eV for 300 s calculated for photoelectrons of similar kinetic energy (see the text above). For the XPS spectra calculation were selected: 728 eV (C 1s and S 2p); 940 eV (O 1s and Sn 3d) and 1026 eV (F 1s) of excitation energies. Due to the lack of calibration (RSFs) for constant photoelectron kinetic energy, the sum of the relative elemental composition of the irradiated films is different from 100% [41, 42].

To gain insights into the fragmentation processes after EUV irradiation, HR-XPS spectra were obtained as a function of the irradiation time. The deconvolution of the C 1s signal data is shown in Fig. 3. From the spectra, it can be observed that the C-S and CF<sub>3</sub> components remain in the surface region even after 10 min of continuous irradiation, a tendency already observed in Fig. 1. Interestingly the CF<sub>3</sub> signals have a shift of about 0.35 eV to the lower binding energies after 30 s irradiation. Because all the spectra were calibrated with the C-C/C-H signal (285.0 eV) and the energy resolution at about 292 eV is 0.1 eV [43], the observed shift is not an artifact. The CF<sub>3</sub> shift to lower binding energies can be understood as a fluorine atom linked to a lower electronegative chemical environment than CF<sub>3</sub>, such as the CH<sub>n</sub>F group types [44, 45]. The C 1s fitting needed to include a new signal at low binding energies (~283.7 eV) that according to previous reports

can be attributed to Sn-C bonds [46, 47]. The spectrum at 30 s of irradiation shows different relative concentrations of components may be due to the presence, on the surface, of adventitious carbon contamination. The fittings of the HR-XPS spectra of the S 2p region also shows that signals that were present at a lower binding energy in the untreated spectrum disappeared after 30 s of irradiation (see Fig. S9 in SI). Fig. S9 in SI also demonstrates the partial loss of the SOx functionalities with the increase of the irradiation time together with the increase in relative concentrations of the S-C. It is necessary to point out that the S=O and SO<sub>3</sub> relative concentrations tend to remain approximately constant after about 5 min of irradiation.



**Fig. 3.** High-resolution XPS spectra of the C 1s envelope of the pristine and irradiated MAPDST*co*-ADSM resist films before and after irradiation by monochromatic synchrotron radiation at 103.5 eV. The irradiation time is indicated in the figure. XPS excitation energy: 368 eV. The intensities of the  $CF_3$  relative concentrations are multiplied by the indicated values for clear presentation.

The HR-XPS spectra of the F 1s signals are more illustrative about the new rearrangements of atoms after irradiation. In previous studies, as commented above, the CF<sub>3</sub> contribution is lost at short irradiations times [7]. This is not the case for the MAPDST-co-ADSM resist films. Fig. 4 shows the dependence of the F 1s HR-XPS spectra on the irradiation time. A new signal is formed after about 30 s of irradiation. This signal corresponds to an emitted photoelectron linked to a lower electronegative environment than the CF<sub>3</sub> functionality, such as it was observed in the controlled fluorination of highly oriented pyrolytic graphite [48]. Additionally, the new F 1s signal has a shift to low binding energies when the irradiation time increased supporting the idea of the existence of important bond rearrangements. Those results show that the high energy of the EUV photons absorbed during irradiation is not enough to cause the complete triflate moiety desorption and dissociation. Additionally, it is necessary to point out that the kinetic energy of the F 1s photoelectron at 728 eV of excitation energy is only about 40 eV. This low kinetic energy of the F 1s photoelectron indicates that the F 1s signal comes from the top surface region.



**Fig. 4.** High-resolution XPS spectra of the F 1s signal of the pristine and irradiated MAPDST-*co*-ADSM resist films before and after irradiation by monochromatic synchrotron radiation at 103.5 eV. The irradiation time is indicated in the Fig. XPS excitation energy: 728 eV.

One important EUV absorption centre is the Sn, which is in a very different chemical environment than the triflate moiety (see scheme 1). HR-XPS spectra were recorded for the Sn  $3d_{5/2}$  and  $3d_{3/2}$  signals and the results are summarized in the Fig. 5. The HR-XPS spectra of Sn 3d show a high efficient oxidation process after irradiation and oxygen exposure. Untreated MAPDST-co-ADSM film shows the HR-XPS Sn 3d<sub>5/2</sub> binding energy at 485.8 eV that matched typical Ph<sub>3</sub>Sn-Ph signals (485.5 eV) and Ph<sub>3</sub>Sn-OH (485.8 eV) [49, 50]. After irradiation and oxidation of the films, two new signals at 487.3 eV and 495.2 eV originated from SnO or SnO<sub>2</sub> are evident. From previous studies it is probable that those signals correspond to the Sn<sup>4+</sup> oxidation state, i. e., SnO<sub>2</sub> [46, 47, 51], Fig. 5 also shows that the maximum intensity of the peak positions of the suggested  $SnO_2$  species move about  $\pm$ 0.3 eV. This energy variation is higher than the 0.15 eV energy resolution of the PGM beamline in the 486-495 eV energy region [43] indicating that those shifts are not artifacts. In the past, there were extensive XPS studies of Sn atoms present in different oxidation states and with different coordination numbers [46, 49, 50]. It is hypothesized that several oxidation estates and coordination of atoms may be present in the signals observed in Fig. 5 that appeared after 30 s of irradiation and remained up to 600 s with minor changes. No desorption of Sn atoms was apparently observed as can be seen in Fig. 1 where a decrease in relative concentration is only observed after 5 min of irradiation mainly due to an increase in the relative concentration of carbon. Those results indicate that the Sn atoms with about 10 times higher atomic absorption cross section than lighter atoms, such as C, O or S [52], remain absorbing EUV photons during all the illumination period. The high energy absorbed may lead to C-Sn cleavage [8, 10, 11], desorption of hydrocarbon fragments [12] and reorganization of bonds, such as Sn-O-Sn or generation of polymerization processes through the Sn–C bond scission [9, 10].



**Fig. 5.** High-resolution XPS spectra for the Sn 3d region of the MAPDST-*co*-ADSM resist films before and after irradiation by monochromatic synchrotron radiation at 103.5 eV. The irradiation time is indicated in the figure. XPS excitation energy: 728 eV.

### 3.2. Near-edge X-ray absorption fine structure.

X-ray absorption spectroscopy is a very powerful tool to probe the surfaces changes of the materials. Therefore, NEXAFS spectra of the carbon *K*-edge of the untreated and irradiated MAPDST-*co*-ADSM at 103.5 eV were acquired and the data are shown in Fig. 6. The main features in the C 1s absorption spectra can be assigned according to previous studies to: C 1s  $\rightarrow \pi^*_{C=C}$  (285.3 eV), C1s  $\rightarrow \sigma^*_{C-S}$  (286.9 eV) and C 1s  $\rightarrow \pi^*_{C=O}$  (288.4 eV) [53, 54]. The absorption signals observed over 290 eV can be assigned to transitions from C 1s to  $\sigma^*_{C-C}$  (293 eV) and  $\sigma^*_{C-F}$  (294.7 eV) unoccupied orbitals [53, 55]. No dependence of the NEXAFS spectra on the SR radiation angle

with respect to the surface was observed (results not shown). Fig. 6 shows that the aromatic rings resisted the irradiation at least during 5 min because the signature transition typical to to  $\pi^*_{C=C}$ , was almost unmodified. A new signal at about 284.3 eV appeared with the increase in the irradiation time. This signal can be identified as the interaction of SnO<sub>2</sub> with carbon double bonds thought Sn-O or Sn-C links which shift the energy of the C 1s  $\rightarrow \pi^*_{C=C}$  transition to lower energy. This surface effect has been previously observed in the investigation between SnO<sub>2</sub> nanoparticles and carbon nanotubes composites [56] and in the reported work on carbon coated SnO<sub>2</sub> nanorods grafted onto graphene [57]. In the case of the C 1s  $\rightarrow \pi^*_{C=0}$  transition it can be seen that the signal became wider than the untreated spectrum indicating that new C=O species were formed in agreement with the XPS results (Fig. 3). The O 1s NEXAFS spectra (see Fig. S10 in SI) show the typical characteristics of the Oxygen K-edge spectra of carbonyl and ester compounds (O 1s  $\rightarrow$  $\pi^*_{O=C}$ ) around 532 eV [58]. In spite of no observation of significant changes for the irradiated films, it is possible to infer a modification of the carbonyl functional groups by EUV irradiation. Fig. S10 (SI) shows that the intensity of the O 1s  $\rightarrow \pi^*_{O=C}$  transition slightly decreased and the peak became wider at longer irradiation times.



**Fig. 6.** Carbon *K*-edge NEXAFS spectra of untreated and irradiated MAPDST-*co*-ADSM resist films for 30, 120 and 300 s. Excitation energy: 103.5 eV.

The high stability of the S 2p shown in Fig.s 1-2 and Table 1, together with the important relative increase in the S-C functionality concentration (see Fig. S9, SI), are a clear indication of the existence of important rearrangements after irradiation. All those secondary reactions apparently avoided the efficient desorption of the sulfur atoms after irradiation. As a consequence, the sulfur L-edge NEXAFS spectra was investigated in more details and the results of untreated and 5 min irradiated MAPDST-co-ADSM resists are presented in the Fig. 7. It is possible to see that the signals at about 166.5 eV (signal 1) and 168.3 eV (signal 2) changed in relative intensities and shapes with the increase in irradiation time (see also Figs. S11-S12 in SI). Similar behavior was observed for the high photon energy signals over 170 eV (Fig. S11 in SI). The first signal in the pristine resist, label 1 in Fig. 7, can be assigned to electronic transitions to the unoccupied  $\pi^*$  orbitals involving the spin-orbit split of the S 2p species  $(2p_{1/2} \text{ and } 2p_{3/2} \text{ levels})$  [59-61]. The second signal at 168.3 eV can be a mixture of several transitions:  $2p_{1/2} \rightarrow \pi^*$ ,  $2p_{3/2} \rightarrow \sigma^*_{C-S}$ ,  $2p_{1/2} \rightarrow \sigma^*_{C-S}$ , and S  $2p \rightarrow empty S 3d$  states [60, 61]. At higher photon energies the signals at about 172.5 eV (signal 3), 175.9 eV (signal 4) and 182.1 eV can be interpreted as higher energy transitions S 2p  $\rightarrow$  empty S 3d and S 2p  $\rightarrow \pi^*_{S=O}$  sulfonic acid functionalities respectively [60, 61]. From the results shown in Fig. 7 and S11 (SI) it can be concluded that there was a general decrease in the sigma transitions, but they still remained up to 5 min of irradiation. It is possible to observe that the electronic transitions to the unoccupied  $\pi^*$  antibonding orbitals involving the spin-orbit split of the S 2p species (signal 1 in Fig. 7) resisted the irradiation. With the irradiation of the resist film, a new signal at about 165 eV (signal 5 in Fig. 7) appeared in the spectra. The signal labeled 5 in Fig. 7 can be assigned to new reduced sulfur

species, such as C–S–C and C–S–S–C [62, 63]. In one of our previous studies of the hybrid n-CAR resist containing the inorganic component  $SbF_6^-$ , the emergence of a new signal was also observed when the irradiation time increased [7]. That signal was interpreted as a new –CH<sub>2</sub>–S–CH<sub>2</sub>– functional group (R–S–(CH<sub>3</sub>)<sub>2</sub> sulfonium) bonded to the phenyl ring.

Fig. 7 shows that in the low energy side region of the sulfur *L*-edge, signals 5 and 1 tend to increase with the increase in the irradiation time (see inset of Fig. 7). On the contrary, the signals label as 2, 3 and 4 (Fig. S11 in SI) decreased continuously with the increase in the irradiation time. Although we have assigned the peaks in the sulfur *L*-edge spectrum taken into account previous experimental results, the assignments can be in some degree speculative due to the existence of several possible molecular configurations. In this type of edges, the molecular orbitals play an important role in the final spectrum shape. Trying to get insight into the origin of the electronic excitations in the sulfur *L*-edge, theoretical simulations using the FEFF9 modeling program [37, 38] were carried out and the results are shown in Fig. 8 together with the experimental spectra for better comparison.



**Fig. 7.** Sulfur *L*-edge NEXAFS spectra of the untreated and irradiated MAPDST-*co*-ADSM resist at 103.5 eV for 300 s. For the interpretation of the signals, labeled 1-5 in the Fig., see text for details. The fittings were carried out using the software package ATHENA [31].

A series of FEFF9 calculations were performed using the two absorbing sulfur atoms: S1 and S36 (see Fig. S13 in SI) that correspond to the sulfur atoms linked to the aromatic ring and to the SO<sub>3</sub> functionality in the triflate moiety respectively. In each of the calculated situations shown in Fig. 8, the electric field vector of the electromagnetic radiation was applied in the three directions of the Cartesian system, which are symbolized by the coordinates of unit vectors (see also Fig. S13 in SI for better visualizing). From Fig. 8 it is possible to observe that the signals labels as 1 and 2 are originated from transitions involving the S1 atom. Signals 3, 4 and 6 are originated from the S36, i.e., the sulfur linked to the aromatic ring and the triflate moiety respectively. The calculated energy difference between the  $2p_{1/2}$  and  $2p_{3/2}$  splitting signals for the S1 is ~ 1.5 eV which agrees quite well with the experimental difference of ~ 1.6 eV. For the calculated signal differences, the

average of the X, Y and Z excitations was taken into account for the comparison with the experimental values. If a similar comparison is made for the signals 3 and 6, the results also agree very well. The experimental energy difference between signals 3 and 6 (see Fig. 8) is  $\sim 9.95$  eV and the calculated difference is  $\sim 10.1$  eV. Notably for the absorbing sulfur atom S1, belonging to the triflate functionality, the FEFF9 calculations show the presence of a transition, probably assigned to  $\sigma^*_{s-C}$ , that may match the energy of signal 5. The signal labeled 5 in Fig. 7 was previously assigned to reduced sulfur species, such as C-S-C and C-S-S-C [62, 63] or a -CH<sub>2</sub>-S-CH<sub>2</sub>- functional group bonded to the phenyl ring [7]. The energy of signal 5 (Fig. 7) after the software ATHENA fitting [31] is 165.1 eV. The calculated average energy (splitting  $2p_{1/2}$  and  $2p_{3/2}$ ) is 164.9 eV which is very close to the experimental value. The calculated signal at 164.9 eV appeared only when the electric field vector of the electromagnetic radiation is in the X direction, which is along the molecular monomer plane. It is hypothesized that this contribution may indicate that the new reorganization of the molecular bonding in the triflate molety is facilitated when the films were irradiated at 103.5 eV. This effect would avoid the total desorption of sulfur and fluorine atoms of the triflate functionality as it was observed in the past.



**Fig. 8.** FEFF9 calculations of the sulfur *L*-edge NEXAFS spectra of the MAPDST-*co*-ADSM monomer unit. The experimental pristine and irradiated NEXAFS spectra of the MAPDST-*co*-ADSM films are shown for comparison on the top. Coordinates X, Y, Z for S1 and S36 represent direction of the electric field vector of the electromagnetic radiation for the sulfur atoms attached to the triflate and aromatic functionalities respectively. The details of the methodology used for the FEFF9 calculations were previously published [27].

## 4. CONCLUSIONS

The experimental evidence obtained in the present work can be summarized as follows:

i. The incorporation of a high EUV absorber centre (Sn) covalently linked in the *MAPDST-co-ADSM* resist exhibited high lithography resolution down to ~12 nm by helium ion beam lithography (HIBL) and ~14 nm by electron beam lithography (EBL) (Fig. S14 in SI). The pre-screening of these hybrid tin resists especially by ebl paves the way for their EUVL since access to EUV photons is scarce. Generally the EUVL

exposure tools and steppers require prior validation by ebl. Thus mechanistic EUV photodynamics and ebl patterning portends these resists as potential EUVL candidates for further patterning.

- ii. The labile triflate moiety was partially lost under EUV irradiation but resisted the EUV absorbed energy up to 10 min of continuous irradiation (F 1s and S 2p signals in Figs. 1, 3 and S9 in SI);
- iii. Absorption of EUV photons led to atoms rearrangements and new functionalities were detected in the surface region (see Figs. 4-7);
- iv. Dissociation of Sn-C and Sn-O with final formation of SnO<sub>2</sub> was clearly observed from the initial time of irradiation (Fig. 5);
- v. FEFF9 theoretical calculation showed the origin of the main sulfur *L*-edge excitations and it may give clues about the bond rearrangement in the resist after irradiation and oxidation.

Irradiation at 103.5 eV (12 nm) of MAPDST-*co*-ADSM resists has shown the loss of the triflate moiety in a much lower degree compared to previous neat poly-MAPDST films studies. Incorporation of the covalent linked organotin compound in the synthesized n-CAR polymer as an absorption centre for EUV irradiation may result in enhanced resolution. It is suggested that the improvement in resolution is due to efficient Sn–O and Sn–C dissociation with important final formation of SnO<sub>2</sub>. The efficient thin oxidation reaction together with the dissociation and bond reorganizations events may allow that an important fraction of the EUV energy absorbed can be used for the formation of new bonds or the initiation of polymerization processes. Those energy-consuming processes may lead to lower fragmentations and desorption rates of the labile components, such as the triflate

functionality. Additionally, after irradiation and oxidation, new carbon functionalities were detected such as C–S and C-F. The present results highlighted the importance of the incorporation of a heavy metal covalently linked to the main polymer structure instead the metal inclusion by electrostatic interaction. Finally, the detailed photodynamic study presented here showed the potential of surface sensitive spectroscopy techniques coupled with theoretical tools to understand basic photofragmentation mechanisms in EUVL.

### **5. ASSOCIATED CONTENT**

**Supporting Information Available:** available free of charge via the Internet at <u>http://pubs.acs.org</u>.: Materials characterization of MAPDST-*co*-ADSM resist: <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR, GPC, EDX, TGA and FTIR. Gaussian09 calculation results. XPS and NEXAFS data dependence on the energy and irradiation time at 103.5 eV.

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Notes

The authors declare no competing financial interest.

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### Highlights

- Organotin resist showed ~ 12-15 nm lithographic resolution by  $e^-$  and  $He^+$  irradiation
- Rearrangements and SnO<sub>2</sub> after EUV irradiation were detected by XPS and NEXAFS
- FEFF9 theoretical calculations confirmed NEXAFS data and gives clues on the mechanism
- The presence of Sn covalent linked to the main polymer structure is highlighted



### **Declaration of interests**

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: