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Electronic structure, excitation properties, and chemical transformations of extreme ultra-violet resist materials

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The electronic structure of extreme ultra violet resist materials and of their individual components, two polymers and two photoacid generators (PAGs), is studied using a combination of x-ray and UV photoemission spectroscopies, electron energy loss spectroscopy, and *ab-initio* techniques. It is shown that simple molecular models can be used to understand the electronic structure of each sample and describe the experimental data. Additionally, effects directly relevant to the photochemical processes are observed: low energy loss processes are observed for the phenolic polymer containing samples that should favor thermalization of electrons; PAG segregation is measured at the surface of the resist films that could lead to surface inhomogeneities; both PAGs are found to be stable upon irradiation in the absence of the polymer, contrasting with a high reactivity that can be followed upon x-ray irradiation of the full resist. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4992083>]

I. INTRODUCTION

Extreme ultra violet (EUV) lithography, using an incident wavelength of 13.5 nm (~ 92 eV), is the primary strategy for future nanolithography.¹ Owing to the weak output of the current EUV sources and high losses from EUV optics, resists of high sensitivity are required. Several strategies have been used to increase organic resist sensitivities, including doping with an element of high ionization cross section such as iodine or fluorine, and inclusion of photo acid generators (PAGs) in the polymer matrix. In such a configuration, EUV photons generate photoelectrons with an efficiency that depends on the atomic cross sections for photo-ionization and on the atomic density. Lower energy electrons are subsequently generated via several energy loss processes until thermalized electrons ($E \ll 15$ eV) are able to react with the PAG components.^{2–4}

Owing to the sensitivity of the resist materials to x-ray or electron irradiation and to their insulating nature, very few spectroscopic studies have been devoted to the electronic structure or the low energy excitation properties of these technologically important materials. Yet, important information could be gathered from a thorough understanding of the electronic properties of these compound materials, including the nature of the low energy excitation processes giving rise to chemical transformations in the resist and the reaction pathways leading to the final chemical products.

In this work, we perform a benchmark electronic structure study of a series of EUV resist and resist component materials. Three sets of samples have been measured: pure polymers (called Polymer 1 and Polymer 2), PAG samples (called S-PAG and I-PAG), and open source resists (OS 2, OS 4, OS 12, and OS 14) based on these polymers and PAGs. The two polymers, whose schematic composition is

indicated in Fig. 1, have been chosen in order to compare the properties of aromatic compounds to aliphatic compounds. Polymer 1 is an aromatic polymer composed of 65% hydroxystyrene (OHStyr), 20% styrene (Styr), and 15% t-butyl acrylate (TBA) in mole percentages. Polymer 2 is an aliphatic polymer composed of 30% methyl adamantyl methacrylate (MAMA), 50% γ -butyrolactone (GBLMA), and 20% a hydroxyl functionalized adamantyl methacrylate (HadMA) in molar percentages. The two ionic PAGs have been widely used in chemically amplified resist work and are represented in Fig. 1. The S-PAG and I-PAG are composed of perfluorobutanesulfonic acid (PFBS) and either triphenylsulfonium (TPS) or tertbutylphenyliodonium (TBPI) anions, respectively, as indicated in Fig. 1. The resist films (OS 2, OS 4, OS 12, and OS 14) are comprised of a combination of each polymer with each PAG as shown in Table I. They were prepared in the following proportions: 83.5 wt. % Polymer, 15 wt. % PAG, and 1.5 wt. % tetrabutylammonium lactate (TBAL) following previous results.⁵

X-ray and UV photoemission spectroscopies have been used to measure the occupied states of these three sets of samples. Ground state electronic structure calculations of simple molecular models chosen to represent the key moieties of the polymers and PAGs have been used to perform a detailed analysis of the photoemission spectra of each compound. Additionally, electron energy loss spectra, using an incident energy of 110 eV, have been measured in order to understand the mechanisms for inelastic electron scattering in such materials. These experimental data are compared to calculated optical absorption spectra of the moieties based on ground state calculations that were validated by their ability to describe photoemission data. Finally, important aspects of resists chemistry, such as PAG segregation at the surface of the resist films, or chemical species created upon irradiation, are investigated using photoemission techniques.

FIG. 1. Polymers and PAG materials considered in this work. The stoichiometry of the different components is indicated in red.

TABLE I. Open source organic resist composition.

	Polymer 1	Polymer 2
I-PAG	OS 2	OS 12
S-PAG	OS 4	OS 14

II. EXPERIMENTAL ASPECTS

A. Sample preparation

All samples were prepared as thin films (20 nm) on highly doped silicon in order to minimize charging effects in photoemission. The films thicknesses were determined using a J. Woollam M-2000 ellipsometer. A Cauchy film model was applied to calculate the film thicknesses for the thin, optically transparent films.

Three sets of samples were studied: two pure polymer films (Polymer 1 and Polymer 2), two films with high wt. % of PAGs (S-PAG and I-PAG), and four open source-resists which are combinations of these materials in the first sample sets in the proportions 83.5 wt. % polymer, 15 wt. % PAG, and 1.5 wt. % TBAL base.⁵

The samples were spun coat onto a silicon wafer under the following conditions: 3700 RPM for 45 s, using a formulation of 1 wt. % total solids in propylene glycol monomethyl ether acetate (PMA). The organic resists and pure polymers films were then baked at 120 °C for 60 s, while the high wt. % PAG films was baked only at 40 °C for 60 s to prevent thermally activated crystallization.

B. Spectroscopic methods

All measurements were performed in an ESCALAB 250xi, without charge compensation, on thin films (20 nm) deposited on highly doped silicon. XPS was performed using a monochromated Al K α line, with an overall resolution of about 0.6 eV. UPS was performed using the He II line, with a resolution better than 0.1 eV. EELS was performed in the

reflection mode in the ESCALAB 250xi using an electron source of 110 eV with a resolution of 1 eV. The spectra have been normalized with respect to the primary peak by setting its maximum to unity. The primary peak centroid has been centered at zero.

All organic samples were thin enough (20 nm film on highly doped silicon substrate) to avoid strong charging effects during measurements. Moreover, spectra were acquired as a function of beam dose to evaluate any chemical transformations induced either by x-ray or electron irradiation. The polymers and the resist samples were quite stable upon x-ray irradiation and for our acquisition times (10 min per core levels). Strong x-ray effects were only observed for the resist compounds. When performing EELS, beam damage was visible for long exposure. Thus, EELS spectra were averaged from short scans (≈ 1 min) acquired on several spots of the samples.

C. Ab-initio methods

Electronic structure calculations of molecules representing the moieties that constitute the polymers and PAGs were performed with the GAMESS(US) software package⁶ using the Becke3-Lee-Yang-Parr (B3LYP) three parameter density functional theory (DFT) theory.⁷⁻⁹ Molecular geometries were at local minima on the potential energy surface calculated with a 6-31 G basis set, except for iodine, for which core levels were simulated using SBKJC effective core potentials.^{10,11} The density of states (DOS) was produced by performing a sum of the individual electronic states convoluted with a 0.7 eV full width at half-maximum Gaussian function. Optical absorption spectra were simulated using the time dependant DFT (TD-DFT) code implemented in GAMESS(US) using B3LYP and 6-31 G. Although the basis set employed here is insufficient to accurately account for excitation energies, the overall nature of the excitations, in particular their relationship to ground-state orbitals, can be retrieved. Only singlet transitions were considered.

TABLE II. Atomic composition expected for the pure polymer films compared to their atomic composition determined using XPS.

Composition	Polymer 1		Polymer 2	
	Calculated (%)	Measured (%)	Calculated (%)	Measured (%)
C	89.2	89.4	77.9	80.2
O	10.8	10.7	22.1	19.8

III. RESULTS AND DISCUSSION

A. Individual components of the EUV resists

1. Polymers

Core level and valence band (VB) spectra of the two polymer thin films were measured using XPS and UPS. For both films, the experimentally determined atomic compositions, obtained using XPS, are found to be close to the expected compositions as shown in Table II.

Core level spectra can often be interpreted using previously assigned chemical signatures from the literature. In contrast, valence band (VB) spectra, obtained either using XPS or UPS, are typically more difficult to interpret due to their complex nature. Nevertheless, VB spectra are also unique chemical fingerprints of organic materials, as they directly reflect the local hybridization. In order to infer the nature of the polymer films from the spectroscopic data, ground state electronic structures of model polymer components have been calculated.

Given that the polymer units are linked by C-C single bonds, and given the typical lack of order in these materials, we have assumed that electron delocalization over the backbone of the polymer chains is not significant. Therefore, the electronic structure of each polymer was simulated using an appropriate linear combination of the electronic structures calculated for the molecules shown in the lower panel of Fig. 2. These particular molecules were chosen, in part, in order to represent the polymer side groups while maintaining the C and O stoichiometry of the polymer. After geometrical

optimization of each molecular unit, the DOS was extracted and used to simulate the DOS of the polymers. To align the calculated DOS to the experimental spectra, rigid shifts were applied to different energy regions (O 1s -11.7 eV; C 1s -7.7 eV and VB 1.6 eV), and individual DOS were then summed with a weight corresponding to the polymer composition. This simple model for the electronic structure is compared to XPS and UPS spectra in Figs. 3 and 4, respectively.

Figure 3 shows the C1s, O1s spectra obtained using XPS. The valence band spectra measured in XPS are reported in Fig. S1 of the [supplementary material](#). The crosses are the experimental data, while the solid black curves are the calculated core level line shapes or valence band DOS. These curves are weighted sums of the individual contributions calculated for each component molecule, which are shown as the colored curves at the bottom of each panel. The bonding configurations associated with each feature in the C 1s and O 1s core levels are indicated.

There is a very good agreement between the core level shapes and the calculated curve for each polymer. The weighted ground state contributions are able to describe the chemical shifts measured in XPS for both the C 1s and O 1s core levels. The C 1s spectra of Figs. 3(a) and 3(b) are comprised of features associated with C-C, C=C and C-H bonds occurring around -284.8 eV and two distinct O-C-C and $-CO_2$ features around -286.8 eV and -288.9 eV, respectively. The O 1s spectra can be decomposed into two main components: one at -533.3 eV associated with C-O-C bonds and a conjugated C=O and overlapping non-conjugated C=O and C-OH features around -532.3 eV.

The XPS valence band spectra of Fig. S1 ([supplementary material](#)) generally agree with the calculated DOS; however, differential cross section effects cause an underestimation of the contribution from O 2s states to the XPS VB spectra in the energy range around -28 eV. In contrast, the cross sections are more balanced in the UPS valence band spectra of the two polymers, shown in Figs. 4(a) and 4(b), which are in very good agreement with their respective calculated DOSs.

FIG. 2. Polymer composition and individual molecular units considered to mimic the polymer electronic structure. The color code for the atoms is as follows: C brown, O red, and H white.

FIG. 3. C1s and O1s core levels measured in XPS (crosses), compared to the calculated ground state DOS for each polymer (black curve). The DOSs calculated for individual components are also shown (colored curves) and specific chemical environments are indicated. When necessary, the * denotes the site related to the peak.

Here again, the calculated DOS has been aligned to the experimental features of the UPS VB spectra. In particular, the presence of the characteristic two-peaked feature measured at -2 eV and -3 eV on polymer 1 and related to phenyl groups is well reproduced in the calculated DOS.

Although the approach taken to model the electronic structure is simple and might not represent finer details (for example there is an inherent over-representation of CH_3 states), the final DOS simulated for the two polymers (either aromatic or aliphatic) enables a deeper understanding of the electronic structure of these polymers. First, these results indicate that the electronic properties of these polymers might not be delocalized, as it could be the case for more ordered, or more highly conjugated systems.

In addition to these photoemission studies, electron energy loss spectra have been measured on the two polymer films for an incident electron energy of 110 eV and are shown in Fig. 5. A striking difference between the two spectra is the presence of an important feature centered around -6.5 eV for the polymer 1 which is absent for polymer 2. For larger energy losses, the loss profile for the two polymers is similar, and consists of a broad feature centered at -17 eV. The narrow peak found around -6.5 eV is typically attributed to π to π^* transitions in benzene-like molecules, explaining the presence of this feature only for the phenolic polymer. The broad loss, however, has been attributed to plasmon resonance losses, due to experimentally observed plasmon-like dispersion in polymers.^{12–14}

FIG. 4. Valence band measured in UPS of both polymers, compared to the calculated DOS.

FIG. 5. EELS spectra measured on the two polymer films for an incident electron energy of 110 eV. The elastic peak intensity has been normalized to 1.

To describe the loss spectra, optical absorption spectra have been calculated for the individual components of each polymers of Fig. 2, and then summed with the appropriate weight corresponding to the polymer composition. The resulting spectra are shown in Fig. S2 of the [supplementary material](#) for the two polymers. As expected, only the phenolic polymer gives rise to an intense absorption feature near 7 eV, arising from π to π^* transitions of the phenyl rings.^{15,16}

As low energy electrons are the key to stimulating chemical reactions in EUV resists, the existence of an important low energy loss process in polymer 1 could open a new channel for production of low energy electrons and therefore increase the EUV resist yield.

2. Photo-acid generators

A study similar to the one that was undertaken for the two polymer films was also performed on polymer films with high PAG concentration. The calculated geometries of the individual ions are shown in Fig. 6. Highly loaded PAG films were obtained by mixing the PAGs with Polymer 2 in a 3:1 weight ratio.¹⁷ However, as shown in Table III, the stoichiometry measured for these films using XPS is strikingly close to what is expected for a pure PAG film. This observation suggests that in both cases the PAG has segregated to the surface of the film. These films are particularly

TABLE III. Atomic composition expected for pure PAG films compared to the atomic composition determined on highly loaded PAG films using XPS.

Composition	I-PAG		S-PAG	
	Calculated (%)	Measured (%)	Calculated (%)	Measured (%)
C	63.2	62.4	61.1	60.7
O	8.0	11.9	8.3	11.6
S	2.6	2.9	5.6	5.1
F	23.7	20.6	25.0	22.7
I	2.6	2.3	...	...

well suited for study of the electronic properties of the individual PAGs.

The C 1s core levels for both PAGs, as well as the calculated core level line shapes for their respective anion and cation counterparts, are shown in Figs. 7(a) and 7(b). Note that the respective alignment of the calculated curves has been chosen so as to match the experimental features due to the intrinsic energy shift related to the Madelung energy in this ionic compound.¹⁸ Three distinct C–F features, corresponding to the CF₃, center CF₂, and S–CF₂ environments of the anion, are found, respectively, at binding energies of –293.6 eV, –291.3 to –290.2 eV, and –288.7 eV. In this region, and superimposed to the CF₂ C1s signal, additional intensity at ~ -291.5 eV is attributed to a $\pi \rightarrow \pi^*$ loss feature from the main C 1s feature at –285.0 eV.

Figure 8 shows the S 2p and the I 3d core levels for the two PAGs. Note that the S 2p level is a spin-orbit doublet split by 1.0 eV, and the I 3d doublet is split by 11.5 eV. As expected, the S-PAG possesses two S 2p core levels, with 2p_{3/2} levels found at –168.8 eV and –167.1 eV, attributed to the R₃–S⁺ and SO₃[–] environments of the cation and anion, respectively. In the case of the I-PAG, a single component corresponding to the anion is observed for the S 2p doublet –168.8 eV, and a single chemical environment is measured for the I 3d level of the cation with the 3d_{5/2} level located at –623.6 eV. The F 1s and O 1s spectra (not shown), which originate from the anion only, were similar for both PAG films. The F 1s core level was found at –688.8 eV and the O 1s was found at –532.8 eV.

FIG. 6. PAG component chemical structure: S-PAG = TPS + PFBS and I-PAG = TBPI + PFBS. Calculated geometries obtained for the individual ions: TPS, PFBS, and TBPI. The color code for the atoms is as follows: C brown, O red, H white, S yellow, F blue, and I green.

FIG. 7. C 1s core levels measured on the PAG films, compared to the DOS calculated for their corresponding anion and cation counterparts.

The VBs measured in UPS on the two PAG films are shown in Fig. 9, along with the calculated DOS for the corresponding anion and cations. Here again, the calculated DOSs have been aligned to experimental features of the VB spectra. By doing so, the nature of the states composing the valence band is easily identified. First, the prominent feature measured for both PAG between -14 eV and -10 eV is attributed to F 2p states from the anion. Additionally, the different shapes obtained for the I-PAG and S-PAG between -7 eV and -3 eV are explained nicely by the different phenyl π systems obtained from the calculated DOS.

EELS spectra obtained from the two PAG-loaded films, acquired with an electron energy of 110 eV, are compared in

Fig. 10. As the EELS spectrum of Polymer 2 does not contain strong features in the region with a loss energy less than 10 eV, most of the EELS signals are thought to originate from the PAGs. Both PAG spectra contain well-defined loss features around -5 eV and -6.5 eV that are expected to be primarily related to phenyl π to π^* transitions. At loss energies greater than 10 eV, both spectra exhibit a broad loss feature centered at -17 eV, resembling the feature identified as a plasmon loss for the two polymers.

Taking an approach similar to the one used to interpret the loss spectra of the polymers, we have calculated the absorption spectra of the individual components of the two PAGs, and then summed the resulting spectra as shown in Fig. S3 of the [supplementary material](#). Again, the calculated spectra, convincingly describe the low energy loss features for the two PAGs. In particular, the loss spectra obtained for the two PAGs appear quite similar and the strong loss features found centered around -7 eV are associated with π to π^* transitions in the phenyl groups of the cation.

To conclude this part, it is important to note that both highly loaded PAG films suffered PAG segregation at the surface. Similar segregation effects, depending on the PAG miscibility in polymers, have been reported previously on other PAG-polymer systems.¹⁹ This allowed a determination of the electronic structure of both PAGs with unprecedented details. As the PAG is a key compound in the EUV chemical reactivity, these results define the basis to study *in-situ* the electronic structure of representative EUV resist materials.

B. EUV resists

1. Resist film composition

The ground state properties and excitation spectra of the organic resist components studied in Sec. III A greatly facilitate the exploration of the four open source resists identified in Table I. As noted earlier, the resist films were prepared using the following stoichiometry by weight: 83.5 wt. % Polymer, 15 wt. % PAG, and 1.5 wt. % TBAL. However, atomic compositions obtained using XPS measurements did not indicate this

FIG. 8. S 2p and I 3d core levels measured on the PAG films, and molecular schematics for the PAG individual components on the PAG.

FIG. 9. Valence band spectra measured in UPS on the highly PAG-loaded films, compared to the calculated DOS of the individual PAG's components shifted appropriately to match experimental features.

FIG. 10. EELS spectra measured on the two PAG films for an incident electron energy of 110 eV. The elastic peak intensity has been normalized to 1.

stoichiometry and signs of PAG segregation were observed for all the resist samples. PAG segregation led to a near-surface composition of 68.8 wt. % Polymer, 30 wt. % PAG, and 1.2 wt. % TBAL, as indicated in Table IV. The concentrations of sulfur and fluorine, markers of the PAGs, allow a clear quantification of both PAGs at the surface of the resist films. The slightly lower percentages of iodine, also a marker for the I-PAG, are likely the result of its higher cross sections for x-ray beam stimulated desorption.

Given that the probing depth of XPS is about 10 nm, and the estimated thickness of 20 nm of the resists films, it

appears that most of the PAG has migrated to the top surface. This behavior was found for all PAG-polymer combinations considered here, and will have a direct impact on the reactivity across the films upon exposure to EUV light.^{20–22}

2. Chemical environment

Given that the PAGs have much higher molecular weights than the polymers (Polymer 1: 118 g mol⁻¹; Polymer 2: 202.4 g mol⁻¹; S-PAG: 562 g mol⁻¹; and I-PAG: 692 g mol⁻¹), the molar composition of these resist materials is dominated by the polymer. This is reflected in the line shapes of the C 1s, O 1s core levels, and VBs of the resist samples measured by XPS as shown in Fig. 11. As can be seen in Figs. 11(a) and 11(b), the C 1s and O 1s core levels of OS 2 and OS 4 resists are comparable to those of polymer 1, while the line shapes from resists OS 12 and OS 14 are comparable to those of polymer 2. The CF_x bond contributions, associated with the PAG anion, occurring at binding energies near -294 eV and -292 eV in the C 1s core levels of Fig. 11(a), are barely visible owing to the low PAG concentration in the polymers. Similarly, the XPS VB spectra are reminiscent of those measured for the pure polymers, with the exception of the presence of prominent F 2s core levels at a binding energy around -35 eV attributable to the anion of the PAGs. All of the F 1s spectra of Fig. 11(d) exhibit the

TABLE IV. Resist film composition as expected from their calculated atomic composition assuming PAG segregation at the surface, compared to the atomic composition determined using XPS.

Composition	OS 4		OS 14		OS 2		OS 12	
	Calculated (%)	Measured (%)	Calculated (%)	Measured (%)	Calculated (%)	Measured (%)	Calculated (%)	Measured (%)
C	82.4	81.3	73.7	71.8	83.6	82.5	74.3	74.6
O	10.2	11.5	18.6	20.8	10.2	11.4	18.8	18.5
S	1.3	1.3	1.4	1.4	0.6	0.8	0.6	1.1
N	0.06	...	0.1	...	0.1	...	0.1	...
F	6.02	5.9	6.3	6.0	5.1	5.1	5.3	5.4
I	...	...	...	...	0.6	0.3	0.6	0.4

FIG. 11. Comparison of the C 1s, F 1s, O 1s core levels and valence bands measured in XPS on the four organic resists OS 2, OS 4, OS 12, and OS 14.

same single feature near -689.1 eV for each resist film, indicating that all fluorine atoms of the anion are in the same chemical environment.

Typical S 2p and I 3d core level spectra, measured for the four resist films, are shown in Fig. 12. For all of the films, the S 2p core levels indicate the presence of the SO_3^- environment of the anion, in agreement with what was measured for the highly loaded PAG films. However, the core levels pertaining to the cations indicate that the cations have undergone partial decomposition. For example, while the I 3d core level spectra of Figs. 12(b) and 12(d) contain an I $3d_{5/2}$ feature at -623.3 eV corresponding to the Ph_2I^+ environment, they also show that another feature at a binding energy of -621.1 eV for both the OS 2 and OS 12 resists, attributable to an iodobenzene (Ph-I) chemical environment. In the S 2p spectra of the OS 4 and OS 14 resists, shown in Figs. 12(e) and 12(f), the expected Ph_3S^+ chemical state observed at a binding energy of -167.0 eV is accompanied by an additional chemical state at -163.7 eV, attributed to a Ph_2S molecular structure.²³

These additional chemical states of I and S found for the cations of the PAGs in the resist films indicate that the PAGs partially decompose upon exposure to x-rays, in a manner consistent with the model shown in Fig. 13 and proposed in earlier work.^{24–30} It is important to note that this transformation was not observed when the highly loaded PAG films were exposed to similar x-ray doses, implying that the chemical conversion of the PAG is mediated by the presence of the polymer. Note that the surface segregation, which led to a PAG concentration of 30 wt. % for the resists, leads to a

local concentration that is still sufficiently low to allow the polymer-mediated PAG photo-decomposition to occur.

EELS spectra measured on the four EUV resist films are compared in Fig. 14. These spectra were obtained as the sum of several low-dose EELS spectra taken on different points at the surface of the films, as it was found that 110 eV electrons would induce transformation of the films more rapidly than the one observed under x-ray exposure. Again, as the molar composition of the resists is dominated by the polymers, it is not surprising that their loss spectra are comparable to the loss spectra measured for the two polymers. Both OS 2 and OS 4 possess the characteristic π/π^* loss, and the PAG, owing to its low molecular concentration, does not contribute significantly to the loss spectra.

3. Kinetics of PAG decomposition under x-rays

Having identified spectral features associated with the two products of the PAG decomposition, it is possible to follow how the chemical reaction proceeds in the resist films as a function of x-ray exposure. The ratio of the intensity of the S 2p and I 3d XPS signals associated with Ph_2S or PhI , to the initial intensities of the Ph_3S^+ or Ph_2I^+ species in the intact PAGs, expressed as a percentage, gives the percentage of decomposed PAGs. This percentage has been measured as a function of x-ray exposure time for the four resist films and the resulting data are presented in Fig. 15(a). In addition, by monitoring the decrease of the integrated S 2p and I 3d XPS intensity as a function of dose, the loss of iodine and sulfur in the resist films was measured as a function of exposure to x-rays and is reported Fig. 15(b).

Figure 15(a) indicates that, upon initial irradiation, for a given exposure time the S-PAG contained in the OS 12 and OS 4 resists undergoes greater decomposition as compared to the I-PAG contained in the OS 2 and OS 12 resists. Moreover, the extent of decomposition is independent of the nature of the polymer. The decomposition of both PAGs saturates, but at different doses. S-PAG decomposition stops after ~ 1000 s, while I-PAG decomposition only stops after ~ 2000 s. The maximum extent of decomposed PAGs is however similar for the four resist materials, approaching a final value of 70%. The saturation could be related to PAG clustering in the polymer matrix, preventing PAG-polymer interaction. This is particularly true in our case, since PAG segregation leads to an effective high concentration of PAG near the sample surface.

H^+ yield upon EUV exposure has been measured for OS 2 (polymer 1 + I-PAG) and OS 4 (polymer 2 + S-PAG) and indicates a very similar behavior (5 ± 0.5 and 4 ± 0.5 H^+ per photon, respectively).⁵ Unfortunately, no similar data exist yet for the OS 12 and OS 14 resists. In our case, upon x-ray exposure, the PAG decomposition seems to occur faster for the S-PAG containing resist than the I-PAG containing resists. These discrepancies could be due to structural inhomogeneities in resist films, given that photoelectron probing depth in photoemission is typically much smaller than UV photon penetration depth, and that S 2p photoelectrons would probe ~ 9.5 nm, whereas I 3d would probe ~ 7.6 nm.³¹

The decomposition kinetics observed for the PAGs under x-ray exposure are correlated with the loss of iodine

FIG. 12. S 2p and I 3d core levels measured in XPS on the four organic resists OS 2, OS 4, OS 12, and OS 14.

and sulfur from the resist materials, as seen in Fig. 15(b). The PAG decomposition is accompanied by the desorption of sulfur and iodine, presumably under the form Ph_2S or PhI . The loss of these products remarkably coincides with the PAG reaction with the resist polymer, indicating that the volatile products of reaction are quite mobile in the resist films and can easily escape as previously thought.³² The percentage of S and I loss for long exposure appears to reach different values for each PAG compound. This could be due to either a sampling depth effect related to the electron mean free path of the I 3d or S 2p core electrons assuming a surface-limited reaction, or to a difference in mobility between the PhI and Ph_2S products in the film. Additional measurements could help understanding film inhomogeneities. For example, angle-resolved XPS could probe PAG segregation or probe trapped species as a function of depth, assuming that resist films are flat enough.

IV. CONCLUSION

This work represents a benchmark study of four open source chemically amplified EUV resist materials using

photoemission spectroscopy and electron energy loss spectroscopy. Using thin films on highly doped silicon substrates, sample charging was limited, and great care was taken in following x-ray and electron beam damage upon irradiation of the samples. As a result, high quality experimental data were obtained and compared to electronic properties calculated using simple molecular models. Several important effects directly relevant to EUV resist material photochemical processes were measured.

Strong energy loss features are found centered around 6.5 eV in the phenolic polymer, originating from π to π^* transitions. Above this transition, the energy loss spectra of phenolic and non-phenolic polymers are remarkably similar. This additional low energy loss channel should provide a pathway for electrons to thermalize faster in the phenolic polymer than in the non-phenolic polymer and could therefore alter electron diffusion and acid production.

Both the iodonium and sulfonium-based PAGs are found to strongly segregate to the surface of the resist films, independently of the polymer used. Therefore, surface inhomogeneities should be expected within a sample depth comparable

FIG. 13. Schematic of the PAG-Polymer decomposition mechanism for the two different PAGs in the presence of a polymer RH.

to the one probed in x-ray photoemission, that is within ten nanometers of the resist films.

Both PAGs were found very stable upon x-ray irradiation, in the absence of polymers. This result contrasts with the high reactivity of the both PAGs in the resist samples, and indicates that the presence of the polymer is necessary to initiate the PAG decomposition in these materials. Additionally, the kinetics of chemical decomposition of the PAGs was measured as a function of x-ray irradiation, and correlated with the loss of the volatile Ph_2S and PhI compounds diffusing out of the resist film.

Other resists are currently studied in order to replace chemically amplified resists such as metallorganic compounds, in part due to the resolution limitation imposed by the acid migration step. The experimental protocol presented

FIG. 14. EELS spectra measured on the four organic resists films for an incident electron energy of 110 eV. The elastic peak intensity has been normalized to 1.

FIG. 15. (a) PAG decomposition in the presence of the polymer under x-ray beam exposure. (b) Iodine and Sulfur loss under x-ray beam exposure with respect to the initial content.

above should be ideal to study novel generation EUV resist materials.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the XPS valence band of pure polymer films, and for the calculated optical absorption spectra of the polymers and of the PAGs.

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