Organotin photoresists for extreme ultraviolet lithography

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Publication date
2019

Document Version
Other version

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Citation for published version (APA):
Chapter 7

The photoreaction mechanism of tin oxo cages under EUV exposure*

In this work, we focus on tin oxo cages as model photoresists and investigate their photoreaction mechanism under EUV (13.5 nm) and DUV (225 nm) exposure. Sn-containing photoresists have attracted attention for EUV lithography because of their high photon absorption cross section at EUV (92 eV, 13.5 nm). We use different X-ray photoelectron spectroscopies combined with mass spectrometry methods to investigate the photon-induced chemistry in the photoresist films. To study primary reactions between EUV photons and the tin oxo cages, photoelectron spectrum with photon energies of 60, 92, 120 and 150 eV were measured. This experimentally confirms the high contribution of tin atoms to the photoionization cross section of the tin oxo cages at 92 eV. Further chemical changes under EUV exposure were also investigated/identified by in-situ and ex-situ measurements such as XPS, time-of-flight secondary ionization mass spectrometry (TOF-SIMS) and resist outgassing measurements. The formation of carbonyl bonds was detected in both in-situ and ex-situ measurement. The EUV induced species were found to be very sensitive to a post-exposure bake step. The outgassing products butane, butene, octane and butanal are detected. Using these results, the chemical reaction mechanism that renders the solubility switch is proposed, making an additional comparison between EUV and DUV photochemistry and reaction yield. This work provides a model to understand the photon-photoresist interaction.

7.1 Introduction

With the progress of the semiconductor industry towards smaller, faster and more powerful next generation chips, EUV photolithography is a much-anticipated milestone because of the short wavelength of 13.5 nm, which enables to shift the frontiers imposed by the optical diffraction limit.\(^1\)\(^-\)\(^3\) To make best use of this technique, not only the design of the photolithographic scanners needs attention, but also the photoresist material used.\(^4\) Chemically amplified photoresists (CARs) based on photochemical acid generation and catalytic deprotection of dissolution inhibiting groups have been widely used in previous generations of photolithography that use 193 nm and 248 nm light sources.\(^5\)\(^,\)\(^6\) CARs, however, have low EUV photon absorption, and weak resistance to etching. Moreover, amplification has to be reduced in order to avoid pattern blur due to acid diffusion, which goes at the expense of sensitivity. As alternatives, inorganic or organometallic photoresists are considered for EUV lithography.\(^7\)\(^,\)\(^8\) The metal atoms in these compounds have a higher photon absorption cross section in the EUV range, possibly removing the need for chemical amplification, and contribute to a strong etch resistance.\(^9\) A variety of metal containing photoresists has been studied, such as Hf-, Zr-, Ti-, and Sn-based materials.\(^10\)\(^-\)\(^16\) Most of them have shown good sensitivity to EUV, and give high-resolution patterns. Among these metal-containing photoresists, Sn-containing materials are attractive owing to their high photon absorption cross section at the EUV wavelength.\(^17\)\(^-\)\(^19\) Recently, Inpria has introduced Sn-based photoresists which are seriously considered for industrial application.\(^20\)\(^,\)\(^21\) Their large EUV absorption coefficient, chemical stability and good pattern performance make Sn-based materials attractive for next generation photolithography.\(^20\)\(^,\)\(^22\)\(^-\)\(^24\)

Different tin-containing photoresists were introduced as potential candidate EUV photoresists.\(^11\)\(^,\)\(^18\)\(^,\)\(^19\)\(^,\)\(^21\)\(^,\)\(^25\) Tin oxo cage compounds can be used as a model to study the photoresist reaction mechanism under EUV exposure due to their easy preparation and well-defined molecular structures.\(^11\)\(^,\)\(^19\)\(^,\)\(^26\) In the present work we focus on the tin oxo cage with n-butyl groups and hydroxide counterions, shown in Fig. 7.1. This class of compounds was first introduced as EUV photoresist by Brainard’s group.\(^11\) They showed that it could be used as a negative tone photoresist, with a resolution of 18 nm dense lines. They also proposed that the homolytic cleavage of the tin-carbon bond, forming a radical at a Sn atom and further cross-linking with the neighbor cage is the main reaction mechanism leading to the solubility switch. In our previous work, the facile cleavage of tin-carbon bonds in the tin oxo cages was supported by quantum-chemical calculations, in which one-electron oxidation or formation of a triplet excited state leads to spontaneous dissociation of the tin-carbon bond.\(^27\) The chemical reaction in the solid thin film under DUV exposure was studied by means of X-ray Photoelectron Spectroscopy
(XPS), which confirmed the loss of carbon experimentally.\textsuperscript{28} Photoexcitation of the bare tin cage dications in the gas phase also led to tin-carbon bond cleavage as the primary process.\textsuperscript{28, 29} It was also discovered that the tin oxo cage can change tone from negative to positive under electron beam lithography and EUV lithography.\textsuperscript{30}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{tinoh.png}
\caption{Structure diagram of TinOH.}
\end{figure}

In the present work, we study the chemical reactions in the tin oxo cage thin films induced by EUV radiation. We investigated the photoionization cross section of the tin oxo cages in the EUV wavelength range. The chemical reaction in the photoresist thin film as a function of EUV dose was studied using X-ray photoelectron spectroscopy (XPS) with in situ exposure. In other experiments, we performed EUV exposure with accurately known doses, and XPS analysis on a separate instrument.\textsuperscript{31} Additionally, the reaction products upon DUV exposure were characterized for comparison. The exposed thin films were further characterized by Time-of-flight secondary ionization mass spectrometry (TOF-SIMS), to study the chemical composition of the final products. To detect low molecular weight reaction products directly, the tin oxo cage resist was exposed to EUV while volatile products were detected using an outgassing qualification tool at IMEC.\textsuperscript{32} The products of the chemical reaction in the tin oxo cages upon EUV exposure were sufficiently evaluated based on all these different measurements. The chemical reaction pathway of tin oxo cages under different EUV exposure doses was quantified and this showed that the chemical reaction yield per photon is higher under EUV than under DUV exposure. The full analysis of this model photoresist’s behavior under photon irradiation gives us the opportunity to find potential ways to build more efficient photoresists and push the EUV lithography toward success.
7.2 Experiment

7.2.1 Sample preparation
The synthesis of the tin oxo cages has been described in our previous publications. In this work we focus on tin oxo cages with hydroxide as counterion (TinOH). For XPS measurements, the substrate should be conductive. To prepare conductive substrates, 2 nm Cr and 18 nm Au were successively coated on 1 × 1 cm$^2$ Si substrates previously cleaned with base piranha (NH$_4$OH/H$_2$O$_2$ solution) using a Leica EM ACE 600 Double sputter coater. TinOH was dissolved in toluene (7.5 mg mL$^{-1}$) and filtered through a 0.25 µm PTFE filter right before spin coating on the prepared conductive substrate at 2500 rpm for 35 s after accelerating by 750 rpm s$^{-1}$. The resulting film thickness was characterized by means of AFM to be ~20 nm. Some samples were pre-exposed by EUV/DUV before measurements. Samples for mass spectrometry were prepared on HMDS pretreated Si and partially pre-exposed by EUV and DUV. Samples for the IMEC resist outgassing system were freshly introduced into the set-up without pre-exposure.

7.2.2 Exposure
In this work, EUV (13.5 nm, 92 eV) exposures were performed at the XIL-II beamline of the Swiss Light Source (SLS) synchrotron at the Paul Scherrer Institute. Deep UV light was produced by a nanosecond YAG-pumped OPA laser (Ekspla NT342B; 225 nm, 2.5 mJ pulse$^{-1}$, 10 Hz). For EUV, 8 × 8 mm$^2$ areas were exposed, while for DUV an area corresponding to the profile of the pulsed laser beam was exposed (diameter ~5 mm). The exposure dose was controlled by varying the exposure time. For the XPS samples, doses of 10, 50, and 250 mJ cm$^{-2}$ were used for EUV exposed samples whereas we chose one dose (50 mJ cm$^{-2}$) to expose with DUV. For the ToF-SIMS analysis, the doses 20, 50 and 125 mJ cm$^{-2}$ were chosen for both EUV and DUV exposures. Since the EUV exposure was done under high vacuum, to get rid of the oxygen and water effects from the atmosphere for DUV exposure, the samples were mounted in a chamber with 225 nm transparent quartz windows filled with dry N$_2$. However, the DUV exposure of the ToF-SIMS samples was performed in air.

7.2.3 Photoelectron spectroscopy
Low dose photoelectron spectroscopy (LowDose PES) was performed using the synchrotron light source (BESSY-II, Helmholtz-Zentrum-Berlin) at the PM4 beamline using an angle-resolved time of flight (ArTOF) spectrometer. A lower photon flux was used in this beamline for probing materials that are sensitive to radiation-induced sample damage. The sample change over time was monitored, and no significant charging or radiation damage was found in the spectra within 10 min. The ArTOF spectrometer makes it possible to record the spectra with high resolution. For our EUVL purpose, at this beamline, by moving a slit out of the
beam, the sample can be exposed to a higher flux of 92 eV photons and followed by the recording of high resolution XPS to trace the chemical changes in the samples without any contamination from the atmosphere. The sample was prepared on a conductive substrate as described above. In this work, we used a 360 l/mm grating, which gives access to the EUV at 92 eV and also allows to measure all the relevant atoms’ chemical high resolution XPS spectra with photon energies up to 650 eV.

In addition to the in-situ measurement, ex-situ experiments were also performed to characterize the photon induced chemical changes. XPS with a SPECS analyzer Phoibos 150, and a monochromatic AlKα X-ray source (photon energy 1486.6 eV, power 200 W, at PSI) was used to investigate the chemical changes in the EUV exposed photoresist thin films. As a comparison, hard x-ray photon electron spectroscopy (HAXPES) was also used to study the DUV exposed photoresist thin films. The details of the HAXPES measurements can be found in our previous publication.²⁸ All peak positions of the core electrons are presented as binding energies and were corrected using the overview spectra, using the C 1s peak at 285.0 eV and the Au 4f⁷/₂ lines at 84.0 eV from a clean Au-foil reference. Fits were performed using Gaussian peaks convoluted with a Lorentzian function (10%), which accounts for the finite lifetime of the core ionized state. Igor Pro software was used for spectra analysis. The element ratio in the sample is in proportion to the corresponded peak area ratio in the overview spectra. By using the software, each relevant peak was integrated individually. Using the relative sensitivity factor for each element from the literature³⁵ the elemental ratio in the thin films can be calculated from the corresponding peak area.

7.2.4 TOF-SIMS mass spectrometry
Time-of-flight secondary ionization mass spectrometry (TOF-SIMS) was conducted on a PHI nano TOF II instrument equipped with a 30 kV bismuth (Bi₃⁺) source. The measured mass range was 0 – 3000 Da. EUV doses of 20, 50 and 125 mJ cm⁻² were applied on 8.5 × 8.5 mm² areas on the samples to be measured.

7.2.5 Outgassing measurement
Unexposed TinOH thin film was prepared and introduced into an IMEC resist outgassing qualification system equipped with EUV light source for exposure, and a residual gas analyzer (RGA) for recording the mass spectrum of the outgassed products.

7.3 Result and Discussion

7.3.1 In-situ XPS
To characterize the photoelectron emission and the chemical changes of the photoresist, various X-ray photoelectron spectroscopy methods were used. As we
observed from the calculation of the photon absorption cross sections of different atoms, the Sn atom was calculated to have strong absorption at around 92 eV, mainly due to ionization of the 4d electrons. To investigate the interaction between the low energy photon (at around EUV range) and the photoresist, low dose X-ray photoelectron spectroscopy was performed on the TinOH thin film. Photon energies 60, 92, 120 and 150 eV were applied and the photoelectron spectra were recorded as shown in Fig. 7.2. All the spectra were corrected for the photon flux, transmission function of the spectrometer and the inelastic mean free path of the electrons with different kinetic energies. In the spectrum, we can observe a clear Sn 4d peak at ~26 eV and a valence band from ~4 to ~12 eV. The Sn 4d orbital is a rich source of primary electrons, which initiate the electron cascades mostly responsible for chemical changes in EUV resists. Comparing the intensity of the Sn 4d peaks at different photon energies, considerably more photoelectrons were generated from Sn 4d with 92 eV photon exposure.

![Figure 7.2](image)

*Figure 7.2. PES of thin layer of tin oxo cage (OH counterions) with photon energies 60, 92, 120 and 150 eV, the intensity of the spectra has been corrected for the photon flux, electron inelastic mean free path and transmission function of the spectrometer.*

The chemical changes in the photoresists upon 92 eV irradiation can be monitored by recording XPS spectra at higher photon energies sequentially. We used 650 eV for overview spectra, 630 eV for high-resolution O 1s spectra, 580 eV for Sn 3d spectra and 380 eV for C 1s. Unfortunately, the photon flux in this set-up at the time of our experiments was not known. Therefore, we used the exposure time to indicate the dose increase, and further tracing the chemical changes. The overview spectra of TinOH under different doses are shown in Fig. 7.3. In line with our
previous work, the relative concentrations of the elements in the thin film are consistent with the expected ratios of tin, oxygen and carbon of 12: 22: 48. As we assumed in our previous work, Sn containing fragments are too heavy to escape from the thin film upon exposure; only fragments containing oxygen and carbon are expected to outgas from the film. This assumption enables studying the change in concentration of O and C as a function of exposure dose, by comparing them to the Sn peaks, as shown in table 7.1. With increasing dose, the oxygen and carbon atom number continuously decreased. The carbon content decreased faster than the oxygen content, but the loss of oxygen is still pronounced. With 10 min exposure, ~2 carbon atoms and ~2 oxygen atoms were removed per tin oxo cage molecule. With 60 min exposure, around 6 oxygen atoms and 30 carbon atoms were removed.

![Figure 7.3](image)

**Figure 7.3.** XPS of TinOH thin layer, unexposed, 10 min and 60 min in-situ EUV exposed. Recorded with photon energy 650 eV.

<table>
<thead>
<tr>
<th>TinOH</th>
<th>Sn</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>12</td>
<td>22</td>
<td>48</td>
</tr>
<tr>
<td>unexp</td>
<td>12</td>
<td>22 ± 2</td>
<td>48 ± 2</td>
</tr>
<tr>
<td>10 min exp</td>
<td>12</td>
<td>20 ± 2</td>
<td>46 ± 2</td>
</tr>
<tr>
<td>60 min exp</td>
<td>12</td>
<td>16 ± 2</td>
<td>18 ± 1</td>
</tr>
</tbody>
</table>

In addition to the XPS overview spectra, high-resolution XPS spectra were recorded to detect the intermediates or the final products in the thin films under EUV exposure. High-resolution XPS spectra provide detailed insight into chemical changes, by looking at differences in electron binding energy in the characteristic orbitals of the different elements in different chemical environments (chemical shift). This adds complementary information to overview spectra, where only the ratio between elements can be studied. The high-resolution spectra of the three
samples at Sn 3d_{5/2}, O 1s, and C 1s positions were recorded using low dose XPS, as shown in Fig. 7.4. To properly interpret the high-resolution spectra, we need to consider the chemical composition of TinOH. As shown in Fig. 7.1, in the original TinOH structure, there are two types of tin atoms: six 5-coordinated tin atoms in the central belt of the cage and six 6-coordinated tin atoms at the caps of the cage. There are three types of oxygen atoms in the cages, 2 oxygen atoms from the hydroxide counterions (OH^-), 14 oxygen atoms bound to three Sn atoms (12 in the central belt of the cage and 2 on the inside) (Sn-O) and 6 oxygen atoms (Sn-OH) from the bridging hydroxides (µ_2-OH) at the caps of the cage. All carbon atoms are located in butyl chains, so that the carbon signal is mainly composed by the core level electrons from sp^3 orbitals. According to DFT calculations,^{38} there are two kinds of carbon atoms in the tin oxo cages structure. The binding energies of the carbon atoms attached to the 6-coordinated tin atom are predicted to be clearly lower than those of all other carbons in the molecule, which have similar binding energies. Therefore, we assume that there are two types of carbon in TinOH in a ratio of 6: 42. Using this assumption, the XPS spectra can be fitted as shown in Fig. 7.4c.

![Graphs showing fitted Sn 3d_{5/2}, O 1s, and C 1s spectra](image)

**Figure 7.4.** Fitted Sn 3d_{5/2}, O 1s, and C 1s spectra of unexposed TinOH (top) and TinOH exposed to 10 min (middle) and 60 min (bottom) of EUV.

As shown in Fig. 7.4a, two sub-peaks contributing to the fitting represent two chemical environments of tin atoms (5-coordinated Sn with high binding energy, 6-coordinated with lower binding energy, according to DFT calculations).^{38} Upon EUV exposure, the ratio of those components could change. However, we assume that these peaks are representative for the chemical changes occurring in the unexposed sample. Using this assumption, the spectra of the EUV exposed samples were fitted using a fixed peak position and bandwidth, so that the fitting was only
affecting the amplitudes. The spectral fits from all the samples were optimized simultaneously. As we see in Fig. 7.4a, the Sn 3d$_{5/2}$ peak corresponding to the unexposed sample is centered at 486.5 eV. Upon increasing exposure time, the peak shifts to lower binding energy (486.2 eV after 10 min) and shifts back to 486.5 eV (after 60 min). The ratio of the two types of tin atoms changed, with the relative number of atoms (12 in total) marked on the sub-peaks in Fig. 7.4a. After 10 min exposure, the higher binding energy sub-peak relatively decreased. After 60 min exposure, the ratio of the two peaks is again close to the original ratio.

For the chemical environment of the oxygen atoms, similarly to the Sn 3d$_{5/2}$ spectra analysis, three sub-peaks are assigned to three chemical environments of oxygen atoms (Fig. 7.4b) (Sn-O, Sn-OH and OH$^-$) in the original TinOH structure. After exposure, there is no obvious shift in the position of the band maximum; the main O 1s peak is almost at the same position, centered at 530.3 eV. However, the shape of the spectrum changes significantly, especially the shoulder around 532.0 eV. Upon 10 min EUV exposure, the sub-peak at the hydroxide counterions position increases, while the Sn-OH sub-peak decreases. Upon increasing the exposure time to 60 min, the components on the high-binding-energy side decreased again.

For the C 1s spectra, the component ratio changes in the spectra are in agreement with the Sn 3d$_{5/2}$ and O 1s spectra analysis. The sub-peaks shown represent the carbon atoms from carbon connected with 6 coordinated Sn (6-Sn-C, green) or carbon connected with 5 coordinated Sn (5-Sn-C) and C-C bonds (blue), respectively, while the red sub-peak represents the carbon atoms from C-O bonds. As shown in Fig. 7.4c, the C-O sub-peak appeared after 10 min of exposure and it decreased again with the higher EUV dose. The O 1s peak from C-O bonds also could be present at around 532.0 eV, which is almost the same position as the OH$^-$ sub-peak. The changes of the sub-peak at 532.0 eV could due to the change of C-O bond.

### 7.3.2 In-situ EUV exposure with detection of outgassing products

To further study which chemical species escape from the film upon exposure, outgassing products were detected with a residual gas analyzer (RGA) using a resist outgassing qualification system at IMEC. TinOH films were prepared on a 4-inch silicon wafer and continuously exposed to EUV with 40 mJ cm$^{-2}$ while scanning a 5 × 5 cm$^2$ area under vacuum. A representative mass spectrum of outgassing products in the $m/z$ range 0 - 300 is shown in Fig. 7.5.
Figure 7.5. Residual mass analyzer (RGA) mass spectrum of the TinOH thin film under EUV exposure.

To analyze the spectra, we compare the peak with the model mass spectra from the NIST database\(^{40}\) where it was found that the outgassing products are likely to be butane (58), butene (56), octane (114) and butanal (72). The mass peak at \(m/z = 207\) could originate from the reagent BuSnOOH with molecule weight 208 from which the tin cages are synthesized. It is unclear whether this compound is already present in the fresh film as an impurity, or whether it is a product of decomposition of the tin oxo cage during exposure.

7.3.3 Ex-situ EUV and XPS

In the in-situ XPS measurement, a photon energy of 650 eV was used for the overview spectra, and the high-resolution spectra were measured with photon energies that give electron kinetic energies near 100 eV. For photoelectrons in this kinetic energy range the inelastic mean free path is around 1.5 nm.\(^{37}\) Therefore, only the very surface of the thin film can be analyzed. Considering the dose contrast curve of TinOH under EUV in previous work (chapter 6),\(^{31}\) we choose 10 mJ cm\(^{-2}\) (under exposed), 50 mJ cm\(^{-2}\) (near dose-to-gel) and 250 mJ cm\(^{-2}\) (overexposed) as the doses for further experiments. Differently from the low dose XPS experiment, where the sample was exposed and measured in the sample chamber under high vacuum (in-situ), we did the exposure and characterization separately (ex-situ). The sample was prepared and exposed at the XIL-II EUV lithography beamline and then
transferred under ambient atmosphere to the Al Kα XPS setup, both at PSI. This means that the sample had the chance to react with oxygen/water during transfer in the atmosphere. In previous work, it was already shown that by adding a post exposure bake step, the sensitivity of TinOH can be improved, probably by reaction of the products of irradiation with O₂ or H₂O in the atmosphere. Here we also studied the effect of the PEB step, which supposedly accelerates the oxidation process of the thin film on the exposed part. For comparison, a 225 nm DUV, 50 mJ cm⁻² exposed sample was also measured by means of HAXPES.

Similarly to the in-situ experiment, the overview spectra, high-resolution Sn 3d₅/₂, O 1s and C 1s spectra were measured. Since the X-ray source is fixed at the energy of Al Kα (1487 eV), all the spectra of the EUV exposed samples were recorded at this photon energy. The inelastic mean free path of the electrons generated with a photon energy of 1487 eV is around 3 nm. Therefore, electrons can be detected from deeper sub-surface layers compared to the measurement with 650 eV or lower photon energies. The DUV exposed sample was measured by means of HAXPES with photon energy 2005 eV. Using the previously made assumption that no tin atoms are lost during exposure, we calculated the area ratio of the different elements from the overview spectra as shown in Table 7.2. Since the samples were exposed to air, reaction with H₂O and O₂ or carbon contamination is possible.

<table>
<thead>
<tr>
<th>TinOH</th>
<th>Sn</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>12</td>
<td>22</td>
<td>48</td>
</tr>
<tr>
<td>unexp</td>
<td>12</td>
<td>22±1</td>
<td>48±2</td>
</tr>
<tr>
<td>EUV 10 mJ cm⁻²</td>
<td>12</td>
<td>22±2</td>
<td>52±3</td>
</tr>
<tr>
<td>EUV 50 mJ cm⁻²</td>
<td>12</td>
<td>25±2</td>
<td>46±2</td>
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<tr>
<td>EUV 250 mJ cm⁻²</td>
<td>12</td>
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<td>33±2</td>
</tr>
<tr>
<td>EUV 50 mJ cm⁻² PEB</td>
<td>12</td>
<td>20±2</td>
<td>42±3</td>
</tr>
<tr>
<td>DUV 50 mJ cm⁻²</td>
<td>12</td>
<td>22±2</td>
<td>41±2</td>
</tr>
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</table>

Upon 10 mJ cm⁻² EUV exposure, the carbon ratio increased slightly, which could be due to the carbon contamination during the transfer. Upon 50 mJ cm⁻² exposure, the amount of carbon decreased, while the oxygen content increased. This could be due to exposure to O₂. Upon 250 mJ cm⁻² exposure, both the carbon and oxygen content decreased. When a post-exposure baking step was added (100 °C, 2 min) after 50 mJ cm⁻² exposure, the oxygen number and carbon number slightly decreased. In the case of 50 mJ cm⁻² DUV exposure, 3.5 × more carbon was lost than with 50 mJ cm⁻² EUV exposure. This number, however, is not very reliable because of the inherent
errors in the numbers (see table 7.2) and the risk of some carbon contamination. The overview spectra of the samples are shown in Fig. 7.6.

![Image](image.png)

**Figure 7.6.** PES of TinOH thin layer, unexposed, 10 mJ cm$^{-2}$, 50 mJ cm$^{-2}$, 250 mJ cm$^{-2}$ EUV exposed, 50 mJ cm$^{-2}$ EUV exposure with PEB, and 50 mJ cm$^{-2}$ DUV exposure. All the spectra from EUV exposures were recorded with photon energy 1487 eV, while the DUV exposed sample was measured with photon energy 2005 eV.

High-resolution XPS spectra were also recorded for this ex-situ experiment, as shown in Fig. 7.7. Using the same assumptions, the high-resolution spectra of Sn 3d$_{5/2}$, O 1s and C 1s were fitted by the same method we used for the in-situ XPS in Fig. 7.4. As shown in the Fig. 7.7a, the Sn 3d$_{5/2}$ peak, instead of shifting to lower binding energy, shifts from 486.8 eV (in the unexposed sample) to higher binding energy, 487.0 eV (10 mJ cm$^{-2}$), 487.0 eV (50 mJ cm$^{-2}$) and 487.1 eV (250 mJ cm$^{-2}$). When a PEB step is added after the 50 mJ cm$^{-2}$ EUV exposure, the peak shifts back to 487.9 eV. With 50 mJ cm$^{-2}$ DUV exposure, the peak also shifts to the same direction to 486.9 eV. The two sub-peaks representing the 5-coordinated Sn (high binding energy), 6-coordinated Sn (low binding energy) atoms were fitted into each spectrum. The fitted ratio between the two types of Sn atoms is marked in Fig. 7.7a.
Using the same assumptions as before, three sub-peaks representing the oxygen atom in Sn-O, Sn-OH and OH\(^-\) were fitted into the spectra. The atomic ratios calculated from the sub-peaks area ratio are marked on the spectra. Compared to the O 1s spectra in Fig. 7.4b, all spectra in the Fig. 7.7b show a large shoulder at the OH\(^-\) range, which could be due to the exposure to air during transfer of the sample. A clear shoulder shows up at the OH\(^-\) sub-peak position (532.4 eV) after a low dose exposure. The reason could be the same as what we observed from Fig. 7.4, where the butyl group connected on the neighboring oxygen atom, forming new C-O bonds, which are located at similar binding energies as OH\(^-\). When the dose was increased to 250 mJ cm\(^{-2}\), the OH\(^-\) shoulder decreased a bit, but the Sn-OH sub-peak increased slightly. With an additional PEB step on the 50 mJ cm\(^{-2}\) exposed sample, the ratio of the OH\(^-\) peak also decreased.

The C 1s spectra were also analyzed after the EUV exposure at the XIL-II synchrotron station and transfer to the spectrometer. Compared to Fig. 7.4c, a larger range was recorded. We found that there is an additional peak at 289.0 eV, representing carbon from C=O. We also studied exposure to DUV (225 nm/5.5 eV,
pulsed laser) and compared this to EUV exposure. It was found that the relative amount of C=O is less under DUV than under EUV exposure.

### 7.3.4 Ex-situ TOF-SIMS

Additionally, time-of-flight secondary ionization mass spectrometry (TOF-SIMS) was used to characterize the EUV and DUV exposed films. This technique utilizes 30 kV ions (Bi$_3^+$) colliding with the film, upon which the ions that come off the surface are measured.\(^{34}\) To compare the different chemical reaction mechanism of TinOH thin film under DUV and EUV, three doses (20, 50, 125 mJ cm$^{-2}$) were chosen to expose the TinOH thin film. As an example, the spectra from the unexposed, and 50 mJ cm$^{-2}$ DUV and EUV exposed samples are shown in Fig. 7.8. For unexposed films, a tin cage ion having lost one butyl group, attached to a hydroxide anion, at $m/z \sim 2397$ was observed in greatest abundance. A small amount of the intact parent ion ([M]$^+$) is detected at $\sim 2436$, while other fragmentation products are also present, such as a tin cage which lost 2 butyl groups ([M-2Bu]$^+$), and the cage without 3 butyl groups but with an extra hydroxide group ([M-3Bu+OH]$^+$). Low mass fragments of the tin-oxide comprising variable elemental formulas [M$_x$O$_y$+H$_z$] were also detected.

**Figure 7.8.** ToF-SIMS spectra of fresh TinOH (blue) and TinOH exposed to 50 mJ/cm$^2$ DUV (225 nm) radiation and EUV radiation (13.5 nm). For comparison, the mass spectrum corresponding to EUV-exposed sample was amplified 25× while for DUV-exposure it was amplified 100×.

By comparing the intensity decrease of the spectra at $m/z \sim 2394$ (see Fig. 7.8), we can compare the reaction yield. Even though ToF-SIMS is generally not regarded as very quantitative\(^{34}\), this can give a reasonable estimation. The intensity of the $m/z \sim 2394$ in the unexposed sample is $1.5 \times 10^4$. It decreased upon exposure. The
intact and near-intact tin oxo cage was observed in far lower abundance for the exposed films relative to unexposed films. For EUV-exposed films, the near-intact tin oxo cage signal could still be detected, but a signal for these species was essentially absent in spectra of DUV-exposed films. Likely, these signals decreased because of cross-linking of different tin oxo cages, leading to large fragments that are outside the range of measurement of the ToF-SIMS instrument.

Weaker signals for bare tin or simple oxides (m/z 100-300) were found in all spectra (see Fig. 7.9). These signals correspond to Sn₃O₇ fragments, which could be singly or multiply protonated. Since these fragments can already be found in unexposed films of TinOH, they are likely formed during the ToF-SIMS. Because the tin oxo cage has an elaborate Sn-O-Sn network at its core, it can be imagined that fragments from this network are extracted towards the detector.

![Figure 7.9. ToF-SIMS spectra in the lower mass range, recorded on a fresh TinOH layer (black), a DUV-exposed layer (blue) and an EUV-exposed layer (red). The spectra were normalized to the first peak (Sn₃O₃H⁺).](image)

For EUV exposed spectra, the peak position of these signals remained the same compared to the unexposed film, while for the DUV exposed film a clear change to higher m/z values was observed. This shift can be seen most clearly for Sn₃O₃H⁺ and Sn₄O₄H⁺. This shift equals an increase of about 16 m/z units. The most likely explanation for this is that some of the tin oxo cages were oxidized upon or after exposure in the open air. For example, the 5-coordinated Sn atom could oxidize, creating an additional Sn-O bond. If Sn₃O₇ fragments are cleaved (as a result of incident Bi₃⁺ ions) after this oxidation has taken place, they may contain an additional oxygen atom.

The ToF-SIMS results suggest that cross-linking occurs for films under both EUV and DUV exposure, and that the reaction to DUV is more efficient than for EUV
using the same energy dose. To quantify these changes, the remaining \( m/z \) 2200-2450 intensity was compared with the unexposed sample, and the remaining percentage was calculated and listed in Table 7.3. If we consider the converted tin oxo cages as the reaction yield, DUV is more effective than EUV exposure. For example, upon 20 mJ cm\(^{-2}\) exposure there is more intact tin oxo cage structure remaining in the EUV exposed sample. With 50 mJ cm\(^{-2}\) DUV exposure, the tin oxo cages seem already fully converted at the sample surface, while there is still around 2\% of intact tin oxo cages remaining after EUV exposure.

**Table 7.3. Percentage of the remaining \( m/z \) 2200-2450 after DUV/EUV exposure.**

<table>
<thead>
<tr>
<th>Exposure dose</th>
<th>EUV % left</th>
<th>DUV % left</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>20 mJ cm(^{-2})</td>
<td>6.5</td>
<td>&lt;0.13</td>
</tr>
<tr>
<td>50 mJ cm(^{-2})</td>
<td>1.9</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>125 mJ cm(^{-2})</td>
<td>&lt;0.07</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

### 7.3.5 Chemical changes upon EUV irradiation

Upon EUV exposure, the primary electrons come mainly from the valence band (\( E_{\text{kin}} \) > 80 eV) or from the Sn 4d band (\( E_{\text{kin}} \) > 60 eV). The kinetic energies of more than 60 eV are high enough for these electrons to further promote chemical reactions in the thin film. In our previous work, using 225 nm DUV irradiation, only a decrease in the amount of carbon was observed, which originates from Sn-C bond cleavage (chapters 3 – 5).\(^{28}\) When EUV is used, primary ionization occurs from atomic and molecular orbitals on Sn, O and C (Fig. 7.10). We may expect, however, that the initially formed ionized species thermalize rapidly, so that the reactions mainly occur from the most stable radical cation, that is, with an electron removed from the highest occupied molecular orbital. The secondary electrons can be expected to ionize mainly the valence manifold, not the Sn 4d orbitals which are shielded by the electron cloud of the molecule. Thus, the starting point is mostly the same for primary and secondary reactions. The emitted electrons will deposit energy in the film and thermalize. They will likely be trapped by tin cage molecules, which, being doubly positively charged, have a high electron affinity. Since the electron mean free path at the initial electron energies is small, the trapping will occur relatively close to the site of origin. Subsequent electron-hole recombination is a quite likely process, which reduces the overall efficiency of the photoreaction. This could explain why the overall quantum yield for the cleavage of butyl groups \( \Phi \sim 0.55 \) (see below) is not high, despite the generation of multiple electrons per photon.
Based on the results from the various experiments, we propose the reaction mechanism of TinOH under EUV as shown in Fig. 7.10. For the purpose of illustration we use a simplified structure representing a fragment of the tin-oxo cages. The primary reaction of the radical cation is the breaking of the Sn-C bond, because the highest occupied MO, from which an electron is removed, has a strong \( \sigma_{\text{Sn-C}} \) character. The butyl radical thus formed could transfer a hydrogen atom producing butene, or react with an active hydrogen atom forming butane, or react with another butyl radical to form octane or the disproportionation products butene and butane. These products were all detected in the outgassing experiment (Fig. 7.5).

Differently from the UV photochemistry, in which a tin-centered radical remains after homolytic cleavage of the Sn-C bond, the tin atom from which the butyl group was lost now has a positive charge. The fate of this tricationic species is not known. In any case it is not a stable molecule that would be detectable in the XPS spectra, because the higher positive charge would lead to a clear increase of the binding energies, which we do not observe. The trication could trap an electron, which would lead again to the same chemistry as in the homolytic photochemical cleavage. Another possible process is deprotonation from a \( \mu_2\)-OH group, alleviating the high positive charge on the cage. In this reaction, the difference between the different counterions with different basicity, which was observed in chapter 5, could play a role. We observe the formation of C-O bonds in the in-situ experiment (Fig. 7.4b), which suggests a structural rearrangement in which a butyl group binds to an oxygen atom. The mechanism for this is not known. A possible structure is shown in Fig 4.7.

**Figure 7.10.** Proposed reactions of TinOH thin film under EUV exposure.

### 7.3.6 Chemical changes in \textit{ex-situ} measurement.

The chemical reaction mechanism under EUV exposure should be the same, regardless of irradiation source. In the \textit{ex-situ} experiment, the sample had the opportunity to react with water or oxygen in the atmosphere during transfer. The direct evidence can be found in Fig. 7.7b, where the O 1s sub-peaks at OH/C-O position from the exposed samples are increased significantly comparing with the...
sub-peak from the in-situ measurement in Fig. 7.4b, which is due to oxygen or water absorbed in, or reacted with, the exposed thin films. As in DUV exposures, oxidation-sensitive low-valent tin compounds or hydrides are probably formed also after EUV irradiation. Upon increasing dose to 50 mJ cm\(^{-2}\), the OH/C-O shoulder increased, as well as the total amount of oxygen in the film. With the EUV dose further increased to 250 mJ cm\(^{-2}\), the exposed cages seem to form a more stable structure than under 50 mJ cm\(^{-2}\) exposure, which has less ability to react with or absorb water or oxygen. When a PEB step is added to the 50 mJ cm\(^{-2}\) EUV exposed sample, the unstable species such as the reacted absorbed oxygen, or water can detach from the thin film, which would explain that the oxygen atom number decreases as shown in Table 7.2 and that the OH/C-O sub-peak also decreases. With 50 mJ cm\(^{-2}\) DUV exposure, the ratio of the OH/C-O sub-peak is also much lower than for EUV exposure at the same dose. The clear C-O sub-peak at \(~ 286\) eV and C=O sub-peak at \(~ 289\) eV in 7.7c indicate that some carbon atoms were oxidized after exposure. It only showed up on exposed samples, and decreased with increasing dose. They decreased when a baking step (PEB) was applied, which indicates that this species is very sensitive to baking. Volatile products (e.g. butanal) could further outgas during PEB, causing this decrease in C and O content. Comparing with the Sn 3d\(_{5/2}\) peak from the unexposed sample, the spectra from all the rest of the samples are shifted to the higher binding energy range, which indicates that more electron withdrawing components are connected with the Sn atom in the cages.

From the element ratio and component ratio in the XPS, we can compare the reaction efficiency of tin oxo cages under EUV and DUV exposure at 50 mJ cm\(^{-2}\) exposure dose. The DUV linear absorption coefficient was measured in Chapter 5, and agrees well with the absorption coefficient in solution; the EUV linear absorption efficient has been measured in previous work\(^{31, 41}\). The same dose was applied on thin films with the same thickness. The absorbed number of photons and the chemical reaction yield are calculated and listed in Table 7.4. The photon energy of DUV is 5.5 eV (225 nm) while EUV has a photon energy of 92 eV, which is 17 times higher. The total absorbed number of DUV photons per molecule is almost 22 times higher than for EUV. The reaction quantum yield can be defined in different ways. In Chapter 3 we estimated the quantum yield for cleavage of butyl chains from the loss of carbon, averaged over a high-dose exposure in air, as \(\Phi \sim 0.015\). If we apply the same definition here we note that 7 out of 48 carbon atoms are lost for 20 DUV photons per molecule absorbed on average. This corresponds to a photocleavage quantum yield of \(\Phi \sim 0.09\) (Bu-group/photon). For EUV exposure with the same dose, only 2 carbon atoms are lost, but the absorbed number of photons is much smaller, resulting in \(\Phi \sim 0.55\). When the PEB is added after the 50 mJ cm\(^{-2}\) EUV exposure, the quantum yield is increased to \(\Phi \sim 1.7\). The DUV
The photocleavage quantum yield found here is considerably higher than the value reported in chapter 3. There we made a crude estimate based on a high conversion, but in the present experiments we used a much smaller conversion, which is more representative of the reactivity of the tin cage. Apparently, the reactivity decreases as more and more butyl groups are lost.

Another way to define the quantum yield is in terms of the number of atoms that undergo a change, as detected in the XPS high-resolution spectra. Then we count the total change of the number of atoms in Sn-C and C-C bonds, and we find that around 0.54 carbon atoms reacted per absorbed DUV photon, about 10.5 carbon atoms reacted per absorbed EUV photon, and with a PEB step added after EUV exposure, this number didn’t change. The photocleavage quantum yield is 0.09 for DUV, which corresponds to 0.36 carbon atoms per photon, so there are 0.18 other reactions per photon. Similarly, the butyl loss quantum yield is 0.55 for EUV, corresponding to 2.2 carbon atoms per photon. Because the total conversion is 10.5 carbons/photon the remaining 8.3 carbon atom/photon are changed but not lost. These are the carbon atoms forming C-O and C=O. When PEB is added, the butyl loss quantum yield is increased to $\Phi \sim 1.7$, corresponding to 6.8 carbon atoms per photon. The additional 4-carbon loss in the PEB step is mainly from the carbon atoms that were oxidized after EUV exposure.

**Table 7.4.** With 50 mJ cm$^{-2}$ DUV and EUV exposure, the absorbed photon number and the quantum yield of the TinOH thin film.

<table>
<thead>
<tr>
<th>TinOH</th>
<th>DUV</th>
<th>EUV</th>
<th>EUV + PEB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs coefficient ($\mu$m$^{-1}$)</td>
<td>18.6</td>
<td>13.5</td>
<td>13.5</td>
</tr>
<tr>
<td>Abs photon/molecule</td>
<td>19.6</td>
<td>0.90</td>
<td>0.9</td>
</tr>
<tr>
<td>C change/abs photon</td>
<td>0.54</td>
<td>10.6</td>
<td>10.6</td>
</tr>
<tr>
<td>$\Phi$ photocleavage (Bu-group/photon)</td>
<td>0.09</td>
<td>0.55</td>
<td>1.7</td>
</tr>
</tbody>
</table>

### 7.4 Conclusion

The photoelectron spectrum of TinOH was recorded with different photon energies. The Sn 4d electrons are a rich source of primary electrons in the Sn-containing photoresists under 92 eV excitation. Comparing with 60, 120 and 150 eV, more photoelectrons are generated at 92 eV photon energy.

High-resolution XPS spectra were measured for tin oxo cages which were exposed to high-energy photons: *in-situ* (vacuum conditions) and *ex-situ* (92 eV photon energy, followed by sample transfer under ambient atmosphere to the XPS instrument). For the *in-situ* measurements, the oxygen content in the sample decreased, while for the *ex-situ* measurements such decrease was not found. This
indicates that oxidation takes place upon bringing EUV-exposed tin oxo cage films under ambient atmosphere. In both the in-situ and ex-situ measurements, formation of carbon-oxygen bonds (C-O) was detected. In the ex-situ measurements, an additional formation of C=O was detected, as a result of reaction with water or oxygen. The C-O/C=O species were found to be very sensitive to a post-exposure bake step.

In an outgassing analysis using a residual gas analyzer (RGA), the outgassing of the carbonyl compound butanal was confirmed. Additional outgassing species included butane, butene, octane and butylstannoic acid. It is unclear whether butylstannoic acid was present in the film as an impurity, or whether it can be removed from the tin oxo cage. This could be relevant because outgassing of metal-containing compounds could lead to non-cleanable contamination on the optics of an EUV scanner.36

The chemical reaction quantum yields under DUV and EUV exposure were calculated and compared at a dose of 50 mJ cm⁻², which is close to the dose required for maximum remaining film thickness after exposure, baking and development. For UV excitation, ~0.09 butyl chains are cleaved per absorbed photon. In terms of quantum yield, EUV excitation is more efficient, giving a loss of ~0.55 butyl chains per photon, which can be increased to 1.7 when PEB is added. This increase is mainly from the cleavage of the EUV irradiation induced species. Per unit energy dose, however, DUV is more efficient. Additional photoreactions are observed upon EUV exposure, however, which increase the total quantum efficiency. Chemical reaction mechanisms were proposed, in which Sn-C bond cleavage is an essential first step. Enabling easier Sn-C cleavage, for instance by using tin oxo cages with different attached organic groups, may improve the sensitivity and resolution of the tin oxo cages.

7.5 References


38. A. M. Brouwer, unpublished result.

