Organotin photoresists for extreme ultraviolet lithography

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Chapter 5

The relationship between photon absorption of tin-nanocages and the efficiency of photochemical reaction*

In this chapter we investigate the UV-photoresponse of tin oxo cages with three different counterions (hydroxide (TinOH), acetate (TinA), trifluoroacetate (TinF)). The tin oxo cages were prepared as thin films and exposed to UV light (225 nm) in a dry N₂ atmosphere. The changes in the UV-vis absorption with exposure dose showed that TinOH and TinA react faster than TinF. This is also reflected in the sensitivity of the films as negative tone photoresists. Synchrotron-based hard x-ray photoelectron spectroscopy (HAXPES) showed that after exposure to a high photon dose more carbon was lost in TinF than in the other two compounds.

5.1 Introduction

The photoresist plays an important role in the development of the photolithography industry. Comparing with traditional organic chemically amplified photoresists (CARs), molecular inorganic materials are attractive because they can easily be used as thinner film, because of their stronger etching resistance and high sensitivity to ultraviolet and extreme ultraviolet (EUV) light. Various molecular inorganic materials as well as nanoclusters and nanoparticles have been investigated. Among those molecular inorganic materials, tin-based molecules are most attractive, due to the high absorption cross section of tin atoms in the EUV spectral range.

Good patterning performance has been achieved by Inpria with tin based photoresist, and Brainard and coworkers studied several Sn-containing molecular materials that showed application potential. Although the Sn containing molecules have been shown to work as photoresists, how photon absorption and the further chemical reaction in the inorganic photoresist leads to solubility change and pattern formation is still unclear.

![Figure 5.1. Tin oxo cages with same cage structure but three different counterions: hydroxide (OH), acetate (A), trifluoroacetate (F).](image)

In this study, we investigated three kinds of tin oxo cages with the same cage structure but three different counterions (hydroxide, acetate, trifluoroacetate) \([(RSn)_{12}O_{14}(OH)_{6}]X_2\), TinOH, TinA and TinF as shown in Fig. 5.1) as model photoresists, to investigate the relationship between photon absorption, the chemical reaction and the solubility change of the photoresist. A 225 nm DUV laser was used as irradiation source. In order to measure the photon absorption of the photoresist in the DUV range, the resists were prepared as thin films on quartz substrates. UV-vis
absorption changes during the DUV exposure were monitored. Additionally, the chemical changes of the photoresist before and after exposure were investigated by synchrotron-based hard X-ray photoelectron spectroscopy. To minimize the effect of oxygen and water, all the exposures were done in dry N₂ atmosphere. By comparing the UV absorption coefficient and the chemical reaction efficiency, the relationship between the photon absorption of the photoresist and the chemical reaction yield of the tin oxo cage photoresists become clearer.

5.2 Experiment

5.2.1 Sample preparation

As in our previous work, tin oxo cages with hydroxide, acetate, and trifluoroacetate as counterions (TinOH, TinA and TinF) were obtained according to the synthesis method described in the literature.¹⁸,¹⁹,²⁰ A structure diagram of the tin oxo cages is shown in Fig. 5.1. UV transparent quartz substrate with thickness 500 ± 20 µm where purchased from SIEGERT WAFER and cut into 1 × 1 cm² squares for the UV-vis absorption measurement. It was cleaned with piranha-base before thin film preparation. Glass coverslips from Menzel Gläser were cut into 1 × 1 cm² squares coated with 2 nm Cr and 18 nm Au layers using a sputter coater (Leica EM ACE 600 Double sputter coater) and used as substrates for X-ray photoelectron spectroscopy measurement. 2-inch Si wafer was purchased from SIEGERT WAFER and it was pretreated with HMDS for photoresist dose contrast curve measurement. The tin oxo-cage materials were dissolved in toluene individually to a concentration of ~7.5 mg mL⁻¹. Solutions were filtered through a 0.25 µm PTFE filter before spin coating on different substrates. Around 20 nm thin films were achieved by spin-coating the solutions with 2500 rpm for 45 s. The spin coated samples were prebaked at 90 °C for 1 min.

5.2.2 Exposure

Exposures were done with a YAG-pumped OPA laser (Ekspla NT342B) which provided nanosecond pulses at 225 nm at 10 Hz (2.5 mJ/pulse). Samples for UV-vis spectroscopy and for dose contrast curves were exposed to 225 nm DUV with a sequence of doses. Samples for HAXPES were exposed to 1.3 J cm⁻². All the exposures were done in a sample chamber with continuously flushing with dry N₂.

5.2.3 Characterization

UV-vis spectra were measured using a Shimazu UV-2600 spectrometer. A Bruker Dimension Icon Atomic Force Microscope (AFM) was used to characterize the thin film thickness. Hard X-ray photoelectron spectroscopy (HAXPES) located at the HIKE end station, BESSY-II, Helmholtz-Zentrum-Berlin was used to record X-ray photoelectron spectra.²¹ In this work, 2005 eV was used as the photon energy. Both
the overview spectra including all relevant lines, and high-resolution spectra of Sn 3d, C 1s, O 1s and F 1s were recorded. All the spectral positions were corrected with the Au 4f\(_{7/2}\) reference at 84.0 eV and the spectra were further analyzed using Igor Pro software.

5.3 Result and Discussion

5.3.1 UV-Vis spectra

The UV-vis spectra of the TinOH, TinA and TinF are shown in Fig. 5.2. All the three tin oxo cages give strong absorption at \(\sim 225\) nm. The samples were exposed to 225 nm laser with a series of doses (from 0 to 3 J cm\(^{-2}\)), and the UV-vis spectrum was recorded immediately after each exposure. The intensity of the main peak at 225 nm continuously decreased with increasing dose. To compare the spectral changes of the three cages, the peak absorbances normalized to the original unexposed sample are plotted in Fig. 5.2d. The intensity decreases of TinOH spectra and TinA are similar, and faster than that of TinF.

*Figure 5.2. UV-Vis spectra of thin films of (a) TinOH. (b) TinA. (c) TinF. (d) peak intensities vs. dose.*

The films thicknesses of the cages on quartz were measured as 20 ± 2 nm. The densities of the thin films were assumed to be the same as the TinOH crystal density.
The absorption coefficients of the three unexposed tin oxo cages can be calculated from the spectra based on Lambert-Beer’s Law. We find that the linear absorption coefficient of TinOH, TinA, and TinF to be 18.8 $\mu$m$^{-1}$, 20.5 $\mu$m$^{-1}$ and 17.8 $\mu$m$^{-1}$ respectively, which are the same within experimental error. When 1.3 J cm$^{-2}$ DUV dose (equal to $1.5 \times 10^{18}$ photons) is used to expose the sample. TinOH, TinA and TinF can absorb $\sim$550 photons/molecule. The decrease of the UV-vis absorption at 225 nm was 48 % for TinOH, 46 % for TinA and 43 % for TinF.

5.3.2 Overview XPS spectra
Thin films prepared from TinOH, TinA and TinF were further characterized by means of HAXPES. The overview spectra of TinOH, TinA and TinF are shown in Fig. 5.3. As expected, the Sn 3d$_{5/2}$ at $\sim$487 eV, O 1s at $\sim$531 eV, C 1s at $\sim$285 eV and F 1s at 688 eV peaks from the photoresist thin films and Au 4f$_{7/2}$ at 84 eV from the Au layer underneath are clearly observed in the spectra. The elemental composition of the three tin oxo cages thin films was verified using the overview spectra, because the peak areas are proportional to the amount of each element present in the sample. We assume the tin atoms do not escape from the thin films during the exposure, so all the other element peaks in the exposed samples were normalized to Sn 3d (equal to 12 Tin atoms). The calculated elemental ratios of the samples are listed in the Table 5.1, where we can see that the atomic composition of the unexposed sample agrees well with the theoretical elemental ratio from the molecules. We also compare the atomic ratio after exposure to a very high dose of UV. In all the three kinds of tin oxo cages the carbon fraction decreased, by 25 % in TinOH, 27 % in TinA and 50 % in TinF. The oxygen number almost stayed the same for all the tin oxo cages. In the TinF, the fluorine atom number decreased from 6 to 3, indicating -CF$_3$ group cleaved and diffused into the N$_2$. If we calculate the chemical reaction efficiency by calculating the carbon atomic ratio change in the tin oxo cages, the chemical reaction yield of the TinF is apparently higher than TinOH and TinA. It didn’t show clear connection between the photon absorption and chemical reaction yield. Since the only difference among the three tin oxo cages is at the counterion part, we can propose the counterion part can affect the chemical reaction yield.

<table>
<thead>
<tr>
<th>Atom</th>
<th>TinOH</th>
<th>TinA</th>
<th>TinF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>Sn 22 O  48</td>
<td>Sn 22 O  52</td>
<td>Sn 22 O  52</td>
</tr>
<tr>
<td>Unexposed</td>
<td>12 22 48</td>
<td>12 24 51</td>
<td>12 24 50</td>
</tr>
<tr>
<td>Exposed</td>
<td>12 22 36</td>
<td>12 24 38</td>
<td>12 24 26</td>
</tr>
</tbody>
</table>
5.3.3 High-resolution XPS spectra

High-resolution Sn 3d spectra of the three tin oxo cages are shown in Fig. 5.4. All the binding energies were calibrated with respect to Au 4f$_{5/2}$ (84.0 eV). For all the tin oxo cages samples, the Sn$3d_{5/2}$ peak positions are at $\sim$487 eV. For unexposed samples, the Sn 3d$_{5/2}$ peak positions are at 487.0 eV (TinOH), 486.9 eV (TinA) and 486.8 eV (TinF). Since all the tin atoms are from the core cage part, which is the same for the three tin oxo cages, the Sn 3d$_{5/2}$ peaks are almost at the same position. But the full widths at half maximum (FWHM) of the Sn 3d$_{5/2}$ band are different: 1.36 eV, 1.29 eV and 1.14 eV, for TinOH, TinA and TinF, respectively. Apparently, the counterions affect the electron distribution in the tin cage via their hydrogen bonding to the bridging OH groups. The difference in the binding energies of the 6-coordinated and 5-coordinated Sn atoms are increased when the hydrogen bond donor is stronger (OH$^-$ > OAc$^-$ > O$_2$CCF$_3$). After the tin oxo cages are exposed to DUV, only the Sn 3d$_{5/2}$ peak position of TinOH slightly shifted to lower binding energy (486.8 eV). The Sn 3d$_{5/2}$ peaks of TinA and TinF stay at the same position. The FWHM of the Sn 3d$_{5/2}$ from three tin oxo cages became narrower, TinOH is 1.27 eV; TinA is 1.17 eV; TinF is 1.13 eV.

By using the same method as in our previous work,$^{23}$ the green sub-peak in Fig. 5.4 represents the 6-coordinated tin atoms in the side part of the cages, and the pink sub-peak represents the 5-coordinated tin atoms in the middle.
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part of the cage. We assumed there are only the two kinds of tin atoms in both the unexposed and exposed samples. After exposure, the ratio between the two sub-peaks was changed as calculated in the Table 5.2.

Figure 5.4. Sn3d $3/2$ spectra of TinOH (a,d), TinA (b,e) and TinF (c,f) before and after exposure in dry $N_2$.

Table 5.2. Relative numbers of two types of tin atoms derived from Sn 3d$_{3/2}$ spectra as well as extracted binding energies of the respective features (see Fig.5.4).

<table>
<thead>
<tr>
<th></th>
<th>atom no.</th>
<th>6-Sn</th>
<th>5-Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>TinOH</td>
<td>BE (eV)</td>
<td>486.7</td>
<td>487.3</td>
</tr>
<tr>
<td></td>
<td>Unexp</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>exposed</td>
<td>9.2</td>
<td>2.8</td>
</tr>
<tr>
<td>TinA</td>
<td>BE (eV)</td>
<td>486.8</td>
<td>487.1</td>
</tr>
<tr>
<td></td>
<td>Unexp</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>exposed</td>
<td>6.7</td>
<td>5.3</td>
</tr>
<tr>
<td>TinF</td>
<td>BE (eV)</td>
<td>486.8</td>
<td>486.9</td>
</tr>
<tr>
<td></td>
<td>Unexp</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>exposed</td>
<td>7.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

By using the same method, high-resolution O 1s spectra of the three cages are analyzed as shown in Fig. 5.5. As shown in the spectra, there is no obvious shifting after exposure. Similarly, three sub-peaks representing the oxygen atoms in Sn-O, Sn-OH and connected counterions (OH$^-$ in TinOH, CH$_3$COO$^-$ in TinA and CF$_3$COO$^-$ in TinF) were fitted in the spectra. In the spectra of the unexposed sample, the three sub-peaks were fitted according to the ratio 14: 6: 2 for TinOH and 14: 6: 4 for TinA and TinF. After exposure, the number of oxygen atoms in all three cages is barely changed. But the shapes of the O 1s spectra are changed,
indicating the chemical environment of the oxygen atoms in the film are changed. As before, we model the spectra with only three kinds of oxygen atoms in the cages after exposure. The contributions of the three sub-peaks are calculated and listed in Table 5.3 together with the binding energy. As shown in Table 5.3, the total oxygen number in the TinOH didn’t change, but the Sn-OH shoulder increased slightly which could due to the hydroxide counterion attach to the cage part further change the chemical environment of oxygen in hydroxide slightly. For TinA and TinF, both the COO⁻ and Sn-OH sub-peaks increased. Since the total oxygen atom number did not change, some rearrangements at the oxygen atoms must have occurred.

![Figure 5.5](image)

**Figure 5.5.** O 1s spectra of TinOH (a,d), TinA (b,e) and Tin F(c,f) before and after exposure in dry N₂.

**Table 5.3.** Relative numbers of three types of oxygen atoms derived from O 1s spectra as well as extracted binding energies of the respective features (see Fig.5.5).

<table>
<thead>
<tr>
<th>atom no.</th>
<th>Sn-O</th>
<th>Sn-OH</th>
<th>COO/OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TinOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>530.7</td>
<td>532.1</td>
<td>533.0</td>
</tr>
<tr>
<td>Unexp</td>
<td>14</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>exp</td>
<td>14</td>
<td>6.7</td>
<td>1.5</td>
</tr>
<tr>
<td>TinA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>530.8</td>
<td>531.5</td>
<td>532.5</td>
</tr>
<tr>
<td>Unexp</td>
<td>14</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>exp</td>
<td>11</td>
<td>8.5</td>
<td>5.0</td>
</tr>
<tr>
<td>TinF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>530.8</td>
<td>531.9</td>
<td>532.4</td>
</tr>
<tr>
<td>Unexp</td>
<td>14</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>exp</td>
<td>14</td>
<td>5.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>
High-resolution C 1s spectra of the three tin oxo cages are shown in Fig. 5.6. Sub-peaks were fitted to the C 1s spectra according to the different chemical environments in the cages. We assumed the main C 1s peak (∼285 eV) originates from CH₂ and CH₃ of the butyl groups and stays at the same position for all the samples, regardless of unexposed or exposed samples. The changes are mainly at the 286.4 eV shoulder from C-O and the peak at around 289.3 eV from C=O. The carbon atoms connected with F have a specific peak around 293 eV. According to our previous work, sub-peaks representing six carbon types 6-Sn-C, 5-Sn-C, C-C, CO, COO and −CF₃ were fitted into the spectra. As shown in Fig. 5.6, the ratio between different C atoms are changed significantly after exposure. In the TinOH spectra, there is a clear peak rising at ∼289 eV, and a shoulder growing up at ∼286 eV. For TinA the shoulder at ∼286 eV becomes much stronger. For TinF, similar with TinA, the shoulder at ∼286 eV becomes more obvious. But the contribution of carbon from the −CF₃ group at ∼293 eV is decreased relative the COO sub-peak. The ratios between the different carbon atoms were calculated and are listed in Table 5.4.

![Figure 5.6](image)

**Figure 5.6. C 1s spectra of TinOH (a,d), TinA (b,e) and TinF (c,f) before and after exposure in dry N₂.**

As shown in Table 5.4, similar with our previous work, apparently, the Sn-C bond cleaved and the generated butyl radical could abstract a hydrogen atom to form butane, or donate a hydrogen atom to form butene. Also, products can be formed with the butyl group attached to O atoms, as shown by the in situ exposure experiments in Chapter 7. In the present experiments, however, some oxygen-containing products could arise from reaction of photoproducts that are sensitive to oxidation during transfer between instruments, in which brief contact with the ambient air could not be fully avoided. These two processes can explain why the oxygen number did not change to a measurable extent, but the C 1s peak shape
changed and the shoulder increased at 286.4 eV. The atomic ratio of carbon from C-O is higher in TinA than TinOH and TinF. We assumed that the counterion could change the electron distribution in the cage part, and the oxygen in the TinA can react with the cleaved butyl radical forming C-O bond easier than in the TinOH. The –CF$_3$ ratio decrease also indicate the counterion could participate in the chemical reaction during the exposure.

**Table 5.4.** Relative numbers of two types of carbon atoms derived from C 1s spectra as well as extracted binding energies of the respective features (see Fig. 5.6).

<table>
<thead>
<tr>
<th></th>
<th>Sn-C</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O/COO</th>
<th>–CF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TinOH</strong></td>
<td>BE (eV)</td>
<td>284.4</td>
<td>285.2</td>
<td>286.4</td>
<td>289.3</td>
</tr>
<tr>
<td></td>
<td>Unexp</td>
<td>6.0</td>
<td>42.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>exp</td>
<td>5.1</td>
<td>26</td>
<td>3.3</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>TinA</strong></td>
<td>BE (eV)</td>
<td>284.4</td>
<td>285.0</td>
<td>286.3</td>
<td>288.8</td>
</tr>
<tr>
<td></td>
<td>Unexp</td>
<td>6.0</td>
<td>43</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>exp</td>
<td>4.8</td>
<td>23</td>
<td>8.7</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>TinF</strong></td>
<td>BE (eV)</td>
<td>284.2</td>
<td>284.9</td>
<td>286.1</td>
<td>289.1</td>
</tr>
<tr>
<td></td>
<td>Unexp</td>
<td>6.0</td>
<td>40</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>exp</td>
<td>4.3</td>
<td>16</td>
<td>3.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

There is no obvious shifting in the F 1s peak from the TinF. The possible reason could be the –CF$_3$ is directly cleaved without any further reaction with the cage and then diffused out into the atmosphere, which is in agreement with what has been observed from the C 1s peak at –CF$_3$ position.

### 5.3.4 Dose contrast curve

Solubility changes of the tin oxo cages were tested by the dose contrast curves. The thin films were exposed with a sequence of doses, and developed using a 2:1 IPA/H$_2$O mixture for 30 s. After development, the film thicknesses were measured with AFM. The dose contrast curves are shown in Fig. 5.7 as plots of the remaining film thickness vs the input dose.

The minimum dose needed to convert the photoresists into fully insoluble are 34 mJ cm$^{-2}$ (TinOH), 40 mJ cm$^{-2}$ (TinA) and 110 mJ cm$^{-2}$ (TinF). The contrast of the three photoresist can be calculated by using the following equation$^{24,25}$:

$$\gamma = \left[ \log \left( \frac{D_l}{D_t} \right) \right]^{-1}$$
Where $D_i$ is the dose induced a negative tone photoresist first to become insoluble and $D_f$ is the dose induced the negative tone photoresist into fully insoluble. The contrasts of the three photoresists calculated from the equation are $2.11 \pm 0.03$ (TinOH), $1.66 \pm 0.01$ (TinA) and $0.96 \pm 0.08$ (TinF). This observation is in line with the UV absorption experiments. The higher carbon loss in TinF after the high exposure dose of 1.3 J cm$^{-2}$ is perhaps not that relevant for the photoresist performance, which in all cases requires < 100 mJ cm$^{-2}$.

The three anions used differ in basicity, nucleophilicity, and hydrogen bond acceptor strength, all increasing in the series $\text{CF}_3\text{COO}^- < \text{CH}_3\text{COO}^- < \text{OH}^-$. Since there is a clear difference in the reactivity we conclude that at some stage of the photoinduced chain of reactions the anion does play a role. It could abstract protons, or bond directly to tin atoms.

![Figure 5.7. Dose contrast curves of TinOH, TinA and TinF under 225 nm DUV exposure.](image)

### 5.4 Conclusions

In this work, the UV photoresponses of three tin oxo cages photoresists with different counterions were compared. The absorption coefficient of the three cages, the chemical reaction yield and the solubility changes in the resist layer were characterized. The UV sensitivity of TinOH and TinA was clearly higher than that of TinF. Since the anions in the former two compounds are more basic and nucleophilic than the trifluoroacetate anion, this suggests that the anions are involved in the chemical process that leads to solubility switching.
5.5 References


