Organotin photoresists for extreme ultraviolet lithography

Zhang, Y.

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Chapter 9

Low-valent Tin Carboxylates as Photoresists*

The interaction of two tin(II) carboxylate compounds, tin(II) 2-ethylhexanoate (Sn[O₂CCH(C₂H₅)(C₄H₉)]₂) and tin (II) acetate (Sn(O₂CCH₃)₂), with ultraviolet and extreme ultraviolet radiation was investigated. Both compounds are sensitive to these types of radiation, and can form insoluble films after light exposure. Resolved line patterns, however, could not be obtained. Investigation of the thin films using IR and XPS spectroscopies indicated that the materials undergo chemical changes during the spin coating process, which adversely affect the solubility. Further processing optimization will be needed before materials of this type can be useful as photoresists.

* We thank Maarten van der Geest and Zhichao Liu for their contributions to this work.
9.1 Introduction

Metal-containing photoresists have become a popular research subject for EUV photolithography due to their high EUV absorption cross-section and potentially high etch resistance. Among all the metal containing photoresists, the tin-containing photoresists have attracted the attention from Inpria, Brainard’s group, Herman’s group, and our own group. The first organotin molecules introduced as photoresist by Brainard’s group are the tin oxo cages. The patterning performance of these materials was well investigated by Brainard’s group and our group. In our previous work, we focused attention on the chemical changes inside the tin oxo cages molecules. Instead of these complex organotin molecules, we here consider the possibility to use smaller tin containing molecules as photoresist. Brainard’s group also investigated dialkyltin(IV) dicarboxylates $R_2Sn(O_2CR')_2$, which are smaller than tin oxo cages. The influences of the $R'$ and $R$ groups on the pattern performance were investigated. Their results indicated the sensitivity of the $R_2Sn(O_2CR')_2$ type of photoresists showed stronger correlation with the $R$ groups than $R'$ groups upon EUV exposure, especially the stability of the $R$ radical. But when the $R$ group is fixed, the higher the molecule weight of the $R'$ group, the lower the sensitivity of the photoresist, except the alkene containing compounds. Their sensitivity and high-resolution pattern ability under EUV exposure have been proven.

Since it is known that ethylhexanoates of several low-valent metals (such as Sn, Zr, Hf, Ti and Sr, etc.) react under UV light, we wondered if Sn(OOCR)$_2$ molecules would be suitable as EUV photoresists. The tin(II) 2-ethylhexanoate (Sn[O$_2$CCH(C$_2$H$_5$)(C$_4$H$_9$)]$_2$) (SnE) and tin (II) acetate (Sn(O$_2$CCH$_3$)$_2$) SnA molecules were chosen as our research items. The bond between the carboxylate group and the metal can break upon UV exposure. The 2-ethylhexanoate radical can decarboxylate and generate CO$_2$ and heptyl radical. From a mechanistic perspective, the chemistry is different from that of organotin compounds because there is no Sn-C bond to be broken. The acetate was considered because it contains a smaller organic fraction, so that photoconversion of the film will lead to smaller shrinkage.

The EUV linear absorption coefficient $\alpha$ can be calculated based on absorption cross sections in the literature and the densities of the materials. The calculated EUV linear absorption coefficient for SnE $\alpha = 6.9$ $\mu$m$^{-1}$, and for SnA $\alpha = 17.5$ $\mu$m$^{-1}$. For tin oxo cage with hydroxide as counterions $\alpha = 13.5$ $\mu$m$^{-1}$. Thus, SnA due to its small organic fraction could potentially give even higher EUV absorption than tin oxo cages.
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The thin film preparation conditions, pattern performances, development conditions and the chemical changes upon exposure inside the thin film were investigated. We obtained the dose contrast curves of the two materials under DUV and EUV irradiation. IR and XPS were used to characterize the chemical changes in the two molecules upon exposure. These two molecules have potential to be used as EUV photoresists, but several questions concerning their stability and processing conditions need further attention.

9.2 Experimental details

Both tin (II) 2-ethylhexanoate (SnE) and tin (II) acetate (SnA) are commercially available from Sigma-Aldrich. SnE is a viscous liquid (melting point < 0°C), and SnA is a white powder. To make use of the two molecules as photoresist they need to be prepared as thin film on substrates. SnE (20 µL) was dissolved in 1 mL hexane and filtered through a 0.25 µm PTFE filter right before spin-coating. It was spin-coated with 2500 rpm for 30 s into 40-50 nm films on single side polished Si substrate (for lithography purpose), on double side polished Si (for FTIR), on Au coated single side polished Si substrate (for XPS), and on quartz substrate (for UV-vis spectroscopy). SnA (30 mg) was dissolved in 1 mL dry ethanol with sonication for 5 min and filtered through a 0.25 µm PTFE filter right before spin-coating. Similarly, the SnA solution is spin coated into 20-30 nm films on different substrates for different experiments as mentioned.

The thin films prepared on the Si wafer were exposed to 225 nm deep UV (DUV) and 13.5 nm extreme UV (EUV). The DUV exposure was performed at ARCNL using a deep UV light source (an Energetiqs EQ-99X Laser Driven Light Source System with a TRIAX190 monochromator). The EUV exposure was performed at the XIL-II beamline of Swiss Light Source (SLS).

UV-Vis absorption spectra of the thin films of SnA an SnE on quartz substrates were measured in transmission mode using a Shimadzu UV-2600 spectrometer. FTIR spectroscopy (Bruker Vertex 80v spectrometer) was used to measure the thin photoresist film prepared on the double side polished Si wafer in transmission mode under vacuum. Attenuated total reflectance (ATR) was measured on the Bruker ALPHA-P compact FTIR spectrometer. X-ray photoelectron spectroscopy (Al Kα based X-ray source) was used to characterize the photoresist film prepared on Au-Cr coated Si substrate. A Bruker Dimension Icon was used for Atomic force microscopy (AFM). The scanning electron microscopy (SEM) was performed using an FEI Verios 460 with a voltage of 1 kV. Thermal gravimetric analysis (TGA) and Differential Scanning Calorimeter (DSC) were performed with a NETZSCH STA 449 F3 Jupiter equipped with automatic sample changer.
9.3 Result and Discussion

9.3.1 Sensitivity of SnE and SnA

The UV-vis absorption spectra of SnE and SnA thin films are shown in Fig. 9.1. It is observed that both of the two compounds give their maximum absorption around 225 nm. Thus, 225 nm is a suitable wavelength to expose the two molecules. The film thicknesses were assumed to be the same regardless of the different substrates, and the linear absorption coefficients of SnE and SnA were estimated as 7.5 and 14.2 $\mu$m$^{-1}$ at 225 nm.

![UV absorption spectra of SnE thin film (a) and SnA thin film (b).](image)

Figure 9.1. UV absorption spectra of SnE thin film (a) and SnA thin film (b).

After the two organotin molecules (SnA and SnE) were prepared into thin films on the Si wafers, we used 225 nm deep ultraviolet exposure and 13.5 nm (92 eV) extreme ultraviolet exposure to test their responses. The contrast curve of DUV exposed SnE gives a good indication of its sensitivity. A 50 nm film of SnE was prepared on a Si wafer and exposed to DUV with a series of doses (from 10 to 2000 mJ cm$^{-2}$) under ambient conditions. After exposure, different developing conditions were tested. At the beginning, the original solvent hexane used for spin-coating was tested as developer, which is a non-polar solvent, but the thin film could not be re-dissolved. In addition, we tried the polar solvents isopropanol and acetone, but neither of them can totally dissolve the unexposed/exposed part of the thin films.

Finally, we found out the development condition as 0.0125% TMAH solution for 30 s followed by rinsing with water for 10 s. After development, the remaining film thickness was measured using AFM. The result is shown in Fig. 9.2.

Unexpectedly, there is still 14 nm film remaining at the unexposed part after development. From the dose contrast in Fig. 9.2, we can see there are three stages. At the first stage (below 100 mJ cm$^{-2}$), the remaining film thickness increases with the dose increasing but the film totally dissolved above 100 mJ cm$^{-2}$. It shows negative tone property at the first stage. At the second stage, from 100 to 600 mJ cm$^{-2}$, the thin film was totally removed and it showed as positive tone pattern. With
the dose continuously increasing to above 600 mJ cm$^{-2}$, it comes to the third stage in which the film thickness increased again and remained at the same thickness up to 2000 mJ cm$^{-2}$. The three stages could correspond to three kinds of products in the thin films, which have different solubility. With the ratio of those three products changing, the solubility of the thin films was changed as three stages. Comparing with the tone inversion controlled by playing with different PEB temperatures in chapter 8, this work realizes dual tone pattern by using SnE in another way.

![Graph](image)

**Figure 9.2.** Remaining film thickness of exposed areas on SnE after development as a function of doses. The initial film thickness (50 nm) and the film thickness of the unexposed part after development (14 nm) are marked in the figure.

In addition to the DUV exposure, EUV exposure was also performed on the SnE photoresist. Since the EUV needs to be performed under high vacuum, a prebake step in the ambient atmosphere with 100 °C 2 min was applied to get rid of the residual solvent before they were transferred into the exposure chamber. After baking, the SnE thin film change from the original viscous oil into solid, which indicated a certain extent of chemical changes. After exposure, the thin film was developed at the same condition, where the sample was dipped in 0.0125% TMAH solution for 30 s and rinsed with water for 10 s. The developed sample was also characterized by AFM. As shown in Fig. 9.3, there was still around 80% of film thickness remaining at the unexposed part, which is around 40 nm. This thick remaining film at the unexposed part makes the whole pattern show as positive tone. Similar with the DUV dose contrast curve, this material seems to present three stages in the EUV dose contrast curve. But unfortunately, a layer of the material remains even for the dose giving the thinnest film after development at around 124 mJ cm$^{-2}$. The developing condition still needs to be optimized.
Figure 9.3. Remaining film thickness of exposed areas of SnE after development as a function of doses. The initial film thickness (50 nm), and the remaining film thickness of the unexposed area after development (40 nm) are also marked in the figure.

Figure 9.4. Deep UV irradiation of SnA. Remaining film thickness of exposed areas after development as a function of doses. The initial film thickness (22 nm), and the two exposed samples developed with different KOH solutions are shown.

Similarly, the performance of SnA was tested under DUV/EUV exposure. The carbon chain in the SnA is much smaller than that of SnE. For the DUV exposed sample, instead of TMAH solution, another alkaline solution was used as developer, which is KOH solution. By using different concentrations of KOH solution combining with different development time (15 s in 0.2% KOH solution or 30 s in
0.1% KOH solution), the dose contrast curve was achieved by measuring the remaining film thickness after developing as shown in Fig. 9.4. Clearly, a negative tone dose contrast curve is observed. At 30 s in 0.1% KOH solution developing condition, the thin film already converted to insoluble at \(\sim 14 \text{ mJ cm}^{-2}\). We can conclude that the dose contrast curve is very sensitive to the developing condition, suggesting that the sensitivity of the SnA can be further improved.

**Figure 9.5.** Comparison between (a) the TGA of SnA as reported in reference 22 and (b) the TGA and DSC result of SnA powder from our measurement.

A PAB step is also needed for SnA films to get rid of the residual solvent. The thermal stability of the SnA was tested. As it is shown in Fig. 9.5a, the TGA results of SnA from the literature,22 mass loss of SnA powder starts at around 65 °C. A different TGA curve was obtained in N\(_2\)-20%O\(_2\) atmosphere on the SnA powder by us as shown in Fig. 9.5b. In our curve the mass starts to drop at around 150 °C, which corresponds with the vaporizing temperature (140 – 160 °C) presented by Maruyama et al.23 The mass loss is associated to an exothermic process, according to the DSC curve in Fig. 9.5b. At the end of the TGA, less material than expected remained (experimental, around 21%; calculated for total conversion to SnO, 57%; for total conversion to SnO\(_2\), 66% ). It seems likely that the SnA is partly vaporized and partly decomposed above 150 °C.24 The differences in the TGA curves could be explained by the different amounts of material used for each experiment (0.3 mg for the experiment in Fig 9.5a, 6.3 mg for the experiment in Fig. 9.5b). A similar phenomenon was observed by Seki et al.22 on \((\text{C}_4\text{H}_9)_2\text{Sn(CHO}_3\text{COO})_2\), where the starting materials could affect the thermal behavior of the sample. The smaller the amount of starting materials was heated, the less mass loss was observed in the end of heating. The reason could be that the smaller amount of tin-containing materials
can be easier to fully oxidize into SnO/SnO$_2$. When larger amounts of materials were used, they can vaporize more before fully oxidizing.

![Graph](image)

**Figure 9.6.** EUV exposure of SnA. The initial film thickness (30 nm) and the remaining layer thickness of exposed areas after development as a function of dose.

Then the SnA was exposed to EUV with a PAB step (100 °C, 2 min). After testing different developers, the EUV exposed sample was developed in 12% TMAH for 10 s and rinsed with water for 10 s. The remaining film thickness was characterized with AFM. The dose contrast curve is obtained as shown in Fig. 9.6. Apparently, it also shows negative tone property.

The results show that both SnA and SnE are sensitive to EUV. The two molecules were tested with EUV interference lithography to see if they can achieve high-resolution patterns. So far, unfortunately, neither of them gave the expected patterns. After development, the EUV interference lithography patterned SnE thin film under optical microscopy is shown in Fig. 9.7.

The bright parts are the 0$^{th}$ order exposed parts, and they were totally removed by the developer. The interference patterns are located as the darker area in the middle of the two 0$^{th}$ order exposed parts. But with the dose increasing, the interference-patterned part was either remained (20 mJ cm$^{-2}$) as a whole piece or removed (84 mJ cm$^{-2}$) as a whole piece after development. When the interference pattern part was characterized with AFM, there was no line structure at all.
Figure 9.7. The developed SnE pattern from EUV interference lithography observed under optical microscopy. The bright areas are the 0th order exposed parts (see Fig 2.3 in chapter 2), and in between each pair of bright areas is the location of the interference pattern. The grey part is the unexposed area.

Figure 9.8. SEM image of developed SnA sample with around 80 mJ cm−2.

Similarly, the SnA sample was exposed to EUV interference. After development, SEM was used to characterize the SnA sample as shown in Fig. 9.8. The whiter part is the exposed part, and the 50 nm half pitch interference pattern should locate at the middle rectangle exposed part. The red square part in Fig. 9.8a was zoomed into Fig. 9.8b, there are not any line structures. Definitely, both SnA and SnE are sensitive to DUV and EUV exposure, but the development conditions need to be optimized to emphasize the solubility difference between the exposed and unexposed parts and achieve high-resolution patterns. Also, the adhesion to the underlayer needs attention.

9.3.2 IR spectroscopy of SnA and SnE

The IR spectrum of the pristine SnE, which is a highly viscous liquid, was measured using ATR-FTIR and used as a reference spectrum for the rest of FTIR measurements. The samples were spin coated as thin films on double side polished
Si substrates and measured in transmittance mode. The IR spectra of different unexposed samples are shown in Fig. 9.9. There is free 2-ethylhexanoic acid as indicated by the COOH stretching at around 1707 cm\(^{-1}\) and the O-H stretching at around 3000 cm\(^{-1}\) in the spectrum (black) of the original liquid SnE, which is very similar to the one shown in reference\(^{16}\). The formation of the free acid could be a result of water adsorption causing hydrolysis:

\[
\text{Sn(OOCR)}_2 + \text{H}_2\text{O} \rightleftharpoons \text{SnO} + 2 \text{HOOCR}
\]

When SnE was prepared as a thin film without any other additional process, the free acid is not present, as shown in the green spectrum in Fig. 9.9. The spectra were normalized to the peak intensity of the CH stretching (antisymmetric and symmetric stretching vibration of \(-\text{CH}_3\) and \(-\text{CH}_2\) at 2962, 2931 and 2869 cm\(^{-1}\)). With a bake step, the COO antisymmetric stretching at around 1562 and 1614 cm\(^{-1}\) disappeared, and shifted to around 1527 cm\(^{-1}\), which could be due to a reorganization of acetate group from monodentate to bidentate chelating upon baking.\(^{25}\) The baked sample prepared at PSI was also measured after one week aging under air atmosphere. As it shows in the blue spectrum in Fig. 9.9, the shape of the spectrum is quite similar with the spectrum from the freshly baked sample. The baked thin film is stable even exposed to the atmosphere for one week.

**Figure 9.9.** IR spectra of SnE liquid measured using ATR (black), freshly prepared SnE unexposed thin film (green), (100°C 2 min) baked SnE unexposed thin film (red) and baked SnE unexposed thin film after one week of aging (blue), measured using FTIR.
In order to follow the chemical changes of SnE under DUV/EUV exposure, FTIR spectra were measured of the DUV/EUV exposed thin films, as shown in Fig. 9.10 and 9.11. The spectra were normalized to the intensity of CH stretching. After DUV exposure, the COO stretching decreased significantly relative to the CH stretch, indicating that the decarboxylation reaction in the SnE dominated after DUV exposure. Although the carbon chain is connected with the carboxylate group, when the decarboxylate reaction happens, it generates a heptyl radical that could react with the tin atom or grab a hydrogen forming heptane remaining in the thin films. That could be the reason why the COO stretching is decreased the CH stretching.

Figure 9.10. IR spectroscopy of unexposed and 200 mJ/cm² DUV exposed SnE samples.

The IR spectra of EUV exposed SnE samples are shown in Fig. 9.11. Since the EUV exposure was performed under vacuum, prebake is needed before the sample was introduced into the exposure chamber. The spectra from the exposed sample are compared with the spectrum from the unexposed-prebaked sample. Similarly, the spectra were normalized to CH stretching at 2962 cm⁻¹. The COO symmetric stretching decreased slightly with the exposure dose increasing, indicating that a small chemical change can already cause the solubility difference.
Figure 9.11. IR spectroscopy of unexposed (100°C 2 min baked) and 20, 50, and 250 mJ cm\(^{-2}\) EUV exposed SnE samples.

Figure 9.12. IR spectra of SnA unexposed thin film (around 24 nm), and films exposed to DUV with doses 10, 50 and 250 mJ cm\(^{-2}\).

Comparing with SnE, the film of SnA is even thinner, namely 20 – 30 nm. Similarly, the IR spectra were recorded on different samples, but the signals from all the samples are quite weak as shown in Fig. 9.12. The spectra were presented as normalized to the COO antisymmetric stretching at 1560 cm\(^{-1}\). As it shows in Fig. 9.12, with the DUV dose increasing, the COO symmetric stretching at 1380 cm\(^{-1}\) increased slightly, indicating that the carboxylate group could be reorganized in the samples.
9.3.3 X-ray Photoelectron Spectra of SnA and SnE

The SnA and SnE thin films prepared on conductive substrates (Au coated Si wafer) were characterized by means of XPS using the spectrometer (chapter 2) operating with a photon energy of 1.4 keV. For the SnE sample, the prebake effect and dose effect were investigated. Since the XPS measurement needs to be done under high vacuum, the freshly prepared SnE sample was kept under atmosphere for 24 h and it turned from viscous oil into solid before it was introduced into the XPS loadlock. This indicated chemical changes such as oxidation or hydrolysis happened in the thin film, which could form a mixture of SnO and SnE before the measurement. The overview spectra are shown in Fig. 9.13. All expected elements in the thin film are present as peaks in the spectra: O 1s at around 531 eV, Sn 3d_{5/2} and 3d_{3/2} at around 486 and 495 eV, and C 1s at around 285 eV.\(^{11,26}\) The small peaks at 84 eV are from the Au layer on the substrate. All spectra were normalized to the Sn 3d peak intensity. After normalizing, we did not see significant changes of the O 1s and C 1s peaks intensity in the exposed sample, but the O 1s and C 1s peaks are clearly decreased due to the pre-baking. The peak area ratio in the spectra corresponds to the element ratio listed in table 9.1.

![Figure 9.13. Overview spectra of SnE unexposed, SnE baked (100°C 2 min) and no prebaked SnE exposed to 225 nm DUV with doses 20, 200, 300 mJ cm\(^{-2}\).](image)

Comparing with the expected ratio, the ratio from the unexposed sample shows a significant difference. The oxygen atom signal is only 50% of what was expected, and the carbon content is even less than half of the expected stoichiometric ratio, presumably due to partial decomposition. The observed elemental ratio is consistent with a film composition of SnO : SnE \(\approx 2 : 1\), where the Sn: O: C ratio is 1: 2: 5.2. There is small decrease of the C 1s and O 1s ratio when we compare the ratio of the unexposed sample and the ratio from the prebaked sample. Based on reference\(^{16}\),
when a photon was absorbed by the SnE molecule, a ligand to metal charge transfer transition would happen, where one electron could be transferred from the ethylhexanoate to the connected Sn$^{2+}$ center into Sn$^+$ and further into Sn atom, which is easy to be oxidized into SnO under air conditions. The electron loss in ethylhexanoate could induce decomposition of ethylhexanoate into CO$_2$ and heptyl radical. With DUV exposure, the oxygen and carbon ratios increased slightly, which is still hard to explain.

Table 9.1. Sn, O and C atomic ratios from samples of SnE unexposed, SnE baked and 20, 200, 300 mJ cm$^{-2}$ exposed to DUV.

<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnE theoretical</td>
<td>1</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>SnE unexp</td>
<td>1</td>
<td>2.0 ± 0.1</td>
<td>5.6 ± 0.3</td>
</tr>
<tr>
<td>SnE unexp_baked</td>
<td>1</td>
<td>1.8 ± 0.2</td>
<td>5.0 ± 0.4</td>
</tr>
<tr>
<td>SnE 20 mJ cm$^{-2}$</td>
<td>1</td>
<td>2.0 ± 0.2</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td>SnE 200 mJ cm$^{-2}$</td>
<td>1</td>
<td>2.8 ± 0.3</td>
<td>6.3 ± 0.5</td>
</tr>
<tr>
<td>SnE 300 mJ cm$^{-2}$</td>
<td>1</td>
<td>2.6 ± 0.3</td>
<td>5.7 ± 0.4</td>
</tr>
</tbody>
</table>

Similarly, XPS was also performed on the unexposed, prebaked, 20, and 100 mJ cm$^{-2}$ exposed SnA samples. The overview spectra of the samples were recorded as shown in Fig. 9.14. The Sn 3d, O 1s and C 1s peaks were clearly observed. To compare the intensity change, we assume that the Sn content does not change during the exposure and measurement. After normalizing the peak intensity to the Sn 3d peak, we can clearly observe that the C 1s peak intensity decreases in spectra from the prebaked and exposed samples, but the intensity of oxygen peak does not change. The peak ratios of all the spectra were calculated and are shown in table 9.2. When we compare the element ratio in the unexposed sample with the theoretical calculation, the oxygen and carbon ratios are lower than expected, as in the case of SnE. The observed elemental ratio is similar with a film composition of SnO : SnA $\approx$ 2 : 1, where the Sn: O: C ratio is 1: 2: 1.3. This indicates the chemical reaction already happened before the samples were introduced into the measurement. With a prebake step, carbon was lost, indicating that the heating promotes the reaction in the thin film. When the DUV exposed samples were checked, the higher the dose, the lower the carbon ratio was observed.
Figure 9.14. Overview spectra of unexposed SnA, prebaked, 20, and 100 mJ cm$^{-2}$ EUV exposed samples.

Table 9.2. Atomic ratios of Sn, O and C from unexposed SnA, prebaked, and EUV exposed samples.

<table>
<thead>
<tr>
<th>Atomic ratio</th>
<th>Sn</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnA theoretical</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>SnA unexposed</td>
<td>1</td>
<td>1.6 ± 0.1</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>SnA unexposed baked</td>
<td>1</td>
<td>1.6 ± 0.1</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>SnA 20 mJ cm$^{-2}$</td>
<td>1</td>
<td>1.6 ± 0.1</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>SnA 100 mJ cm$^{-2}$</td>
<td>1</td>
<td>1.8 ± 0.2</td>
<td>0.4 ± 0.1</td>
</tr>
</tbody>
</table>

Above all, we confirmed that there were chemical changes in the SnA and SnE thin films upon prebake and exposure. The photolysis mechanism of SnE has been presented in the literature and is adapted here as Fig. 9.15a.\textsuperscript{16} In reference 16, the photolysis products could be SnO, CO, CO$_2$ and hydrocarbon molecules. Additionally, the SnA and SnE could be hydrolyzed as proposed in Fig. 9.15b. The molecules have the opportunities to react with water and generate SnO or the intermediate HOSnCOOR, which could mix with the original molecules and lead to the difference between the measured and expected atomic ratio in XPS measurements. Since all the reactions in Fig. 9.15 are possible, the final remaining thin film could be a mixture of SnO, RCOOSnOH and Sn(COOR)$_2$, which is consistent with the XPS result that there is always carbon remaining after different processes.
Figure 9.15. (a) Proposed chemical reaction mechanism of SnA and SnE upon exposure, figure from reference 16. (b) Hydrolysis of the tin(II)carboxylates.

9.4 Conclusion

In this work, we investigated two small molecules SnE and SnA as EUV photoresists. We could demonstrate the sensitivity of the two materials under DUV and EUV exposure. We manage to develop the DUV/EUV exposed SnE and SnA samples by using either TMAH or KOH solution as developers. More efforts are needed to find better process conditions for high-resolution patterning. Evidence was found that chemical changes occurred when the compounds were deposited as thin films. Baking has a significant effect on the molecular composition. Based on the IR results, decarboxylation can happen in the SnE thin films upon bake and DUV exposure. To understand the chemical changes inside the thin film could help us get better understanding on the properties of the unexposed and exposed materials, which is important for developing proper process conditions.

9.5 References


Summary

Photoresists are photosensitive materials that are used to transfer patterns in photolithography. New types of photoresists are needed for the next generation of photolithography, which uses extreme ultraviolet radiation (EUV, wavelength 13.5 nm). Organotin materials have drawn great attention in the photoresist field, not only due to their potential in industrial application but also because of the interest from the fundamental point of view. This thesis focuses on two kinds of organotin materials as photoresists: the tin oxo cages and tin(II) carboxylates molecules. We study the interaction of EUV and short-wavelength (deep) UV (225 nm) photons with the two types of photoresist candidates.

Chapter 1 gives an overview of the subjects of photolithography and photoresists. The developments of photolithography and photoresists are briefly summarized. Some metal-containing photoresists and their proposed reaction mechanisms are discussed. The organotin type of photoresists is attractive for us as a prototype for the study of the chemical reactions on metal containing photoresists upon light exposure. This is important for understanding the principles of EUV-induced chemical reactions, and can form the scientific groundwork for the optimization of metal-containing photoresist performance in the next generation photolithography.

In Chapter 2, we introduce the experimental techniques we used throughout the thesis. Various X-ray photoelectron spectroscopy (XPS) techniques that we used receive special attention, because they uniquely enable the characterization of the chemical reaction in the photoresist thin films.

The DUV photon-induced chemical changes in tin oxo cages are studied in Chapters 3, 4 and 5 by using the HAXPES technique (Hard X-ray Photoelectron Spectroscopy). In Chapter 3, based on the HAXPES spectra from the tin oxo cages with hydroxide counterions (TinOH) upon DUV exposure, we find direct evidence indicating that the Sn-C bonds in the tin oxo cages are cleaved upon DUV exposure. By comparing the chemical reaction of the tin oxo cages under dry nitrogen (N\textsubscript{2}) and air atmosphere, we find that the average photochemical reaction yield of TinOH at high conversion is higher under air than in an atmosphere of N\textsubscript{2}, but rather low (~1 %) in both cases. A reaction mechanism of TinOH photoresist exposed to DUV is proposed.

In chapter 4 we show that not only photons introduce chemical changes in the photoresist. Thermal processes in air after exposure (baking processes) cause chemical reactions in the tin oxo cages which further reduce the solubility. These
reactions occur at temperatures where the intact non-exposed film is thermally stable, and can be used to enhance the sensitivity (see Chapter 6). The photochemical reactions under nitrogen probably lead to a partial reduction of the tin cage, while the baking processes lead to oxidation, and more cross-linking of the tin cages.

In Chapter 5, the relationship between the DUV photon absorption and chemical reaction yield in the photoresist is further investigated by comparing three types of tin oxo cages, which have the same cage structure but three different counterions (hydroxide (TinOH), acetate (TinA), trifluoroacetate (TinF)). The chemical reaction yields of the three cages were evaluated through XPS and UV-absorption spectra. The solubility changes in the resist layer were quantified by constructing dose-contrast curves. The sensitivities of TinOH and TinA are similar, and higher than that of TinF. This provides evidence that the anions must be involved in some stage of the chemical process that leads to solubility switching. Interestingly, the weaker basicity and hydrogen bonding ability of the trifluoroacetate anion compared to acetate and hydroxide is reflected in the Sn 3d XPS spectra.

The EUV patterning abilities of the tin oxo cages are investigated in Chapter 6 and Chapter 8. The tin oxo cages can generate negative tone patterns as discussed in Chapter 6. The pattern performances of the tin oxo cages with different counterions (TinA and TinOH) under EUV exposure are studied. The results indicate that the sensitivity and the quality of the patterns can be affected by the counterions (hydroxide (TinOH), acetate (TinA) and malonate (TinM)). A possible reason is their physical properties are modified by the counterion such as the solubility. The results of Chapter 5 (which were obtained after the results from Chapter 6 were published), however, show that there is an effect of the counterions on the chemical reactivity in the DUV photochemistry, and this difference may also affect the EUV-induced reactions. The sensitivity of the photoresist can be improved by optimizing the process conditions, such as film thickness, post-exposure baking (PEB) temperature and development conditions. The thermal stability of the TinOH powder is characterized by TGA measurement, and it is shown to be stable at least until 100 °C. By comparing the pattern performance under different PEB temperatures, 100 °C is chosen as the proper PEB temperature for the TinOH to generate negative tone patterns. We also observed that the sensitivity and pattern resolution of the TinOH photoresists are improved by adding a PEB step. After a partial optimization, we achieved a 22 nm half pitch pattern with 57 mJ cm⁻² EUV dose by using TinOH as photoresist. A 30 nm half pitch pattern with 57 mJ cm⁻² EUV dose is realized by using TinA as photoresist.

The EUV photon-induced chemical changes in the tin oxo cages are systematically investigated in Chapter 7. The reaction mechanism of the tin oxo cages under EUV
is compared with the mechanism under DUV exposure. Different forms of XPS combined with mass spectrometry are used to investigate the photon-induced chemistry in the photoresist films. The photoemission spectrum of TinOH with photon energies around 92 eV is reported for the first time, where we confirm that the core-level electrons from Sn 4d orbitals are an effective source of primary electrons under EUV exposure. The photolysis-outgassing products (gaseous compounds that are released from the film) under EUV exposure are characterized by an outgassing system in collaboration with IMEC. Butane, butene and butanal are generated if TinOH is exposed to EUV, which further confirms that the Sn-C bond can be cleaved upon EUV exposure, as deduced from our XPS analyses. The DUV/EUV exposed TinOH thin films were analyzed by means of XPS and mass spectrometry. The chemical reaction quantum yield was found to be higher with EUV exposure than with DUV exposure. A reaction mechanism of the tin oxo cages upon EUV exposure is proposed.

As an extension of the research of Chapter 6, we found that dual-tone patterns can be realized by using the tin oxo cages as photoresist under high PEB temperature (150 °C), and this phenomenon is further explored in Chapter 8. The normal (negative tone) pattern is observed for TinOH with PEB temperature below 150 °C as shown in Chapter 6. When the PEB temperature reaches 150 °C, however, varying the exposure dose can reverse the tone of the pattern. This dual tone phenomenon is observed with EUV and E-beam exposure. By analyzing the sample with TGA and XPS, we related this phenomenon to the water loss occurring on the unexposed TinOH at this temperature.

In Chapter 9, we study the possibility of using tin(II) carboxylate compounds as EUV photoresists. The patterning performance and the chemical reaction of tin(II) acetate and tin(II) ethylhexanoate thin films upon DUV/EUV irradiation are studied. The sensitivities of the two molecules under DUV/EUV exposure are demonstrated. Post application baking has significant effect on the molecular composition. Both of the two molecules show clear chemical changes upon light exposure. High quality pattern, however, could not (yet) be achieved by using these two materials as photoresist.