EUV Mechanistic Studies of Antimony Resists

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We have developed a method to study the photomechanism of our antimony carboxylate platform Ph3Sb(O2CR)2. A series of mechanistic studies followed the production of reaction byproducts by mass spectrometer, as they leave the film during exposure to EUV photons or 80 eV electrons. The major volatile products are CO2, benzene and phenol. The rate of outgassing is well-correlated with the reaction energy of decarboxylation of the carboxylate ligand as determined by density functional theory. Additionally, a deuterium labeling study was conducted to determine the source of hydrogen needed to convert phenyl and phenoxy to benzene and phenol. Specifically, EUV exposure of Ph3Sb(O2CCD3)2 creates d0-benzene and d1-phenol with >95% isotopic purity. Several mechanistic pathways are proposed and discussed.

Keywords: EUV, Photoresist, Outgassing, Mechanism, Antimony, Deuterium Labeling

1. Introduction

Today, the microelectronics industry maintains Moore’s law at the 14-nm node through the use of multiple patterning with 193-nm immersion lithography. To extend Moore’s law through the 10-nm node and beyond, this industry is expected to implement extreme ultraviolet (EUV) lithography into high volume manufacturing. However, several technological hurdles must be overcome before the implementation of EUV is possible [1-3]. Photoresist performance, in particular, must improve dramatically before EUVL can be used in the manufacture of IC devices [4]. Many new resist platforms have been explored in recent years, to find pathways for the dramatic impact in lithographic performance.

Metal-containing resists are some of the most exciting platforms being explored today by resist companies around the world. The successes of Inpria (tin-based) and Cornell (hafnium oxide based) resists [5,6] were initial inspirations for our group’s project called Molecular Organometallic Resists for EUV (MORE). This work has produced multiple organometallic resists platforms [7-12].

One of our most exciting negative-tone resist platforms is composed of antimony complexes containing polymerizable olefins [10]. Ph3Sb(O2C=CH2)2 (JP-20, Fig. 1A) is a prominent representative of this platform and prints 35-nm dense lines with extremely high photospeeds of 5-9 mJ/cm2. We have synthesized and lithographically evaluated dozens of derivatives of JP-20 all containing some polymerizable olefins.

Fig. 1. Three pentacoordinate antimony carboxylate MORE resists (A) Ph3SbAcrylate2 (JP-20), (B) Ph3SbAcrylate2 (JP-18), (C) a generic representative of this platform, Ph3Sb(O2CR’)2.

The bulk of our experimental results point to the predominant mechanism for EUV exposure to be free-radical polymerization [10]. However, one study, in particular, indicates that free-radical polymerization is only part of the story behind the mechanism of the antimony MORE resists. A
direct comparison of contrast curves of **JP-20** [Ph$_3$Sb(O$_2$C=CH$_2$)$_2$] and **JP-18** [Ph$_3$Sb(O$_2$CCH$_3$)$_2$] shows that JP-20 is only 3-5 times faster than JP-18 (Figs. 1 and 2). This is quite surprising given that JP-18 does not contain polymerizable olefins. Clearly, there exists an underlying mechanism at work for an antimony complex of the general type of Ph$_3$Sb(O$_2$CR')$_2$ (Fig. 1C) that operates independently of olefins. Furthermore, in order to fully understand the mechanisms of our olefin-containing mechanisms, we must first understand the mechanisms of the antimony complexes that **do not contain olefins**. Here, we present several mechanistic studies directed at understanding the photochemical interaction of EUV photons with antimony carboxylate resists.

2. Results and discussion

2.1. Reaction product identification

To better understand the chemistry occurring during exposure, we identified outgassed reaction products generated during photolysis via mass spectrometry [13-15]. In our initial experiment, we exposed a film of JP-18 to EUV and collected the positive-ion mass spectral data (Fig. 3). Prominent peaks were observed at 44, 78 and 94 amu; they were identified as carbon dioxide, benzene and phenol respectively [16-18]. Additional peaks were observed at 152-154 amu indicative of biphenyl [19]. Due to the low diffusivity of this species through film, further investigation of the production of biphenyl was not carried out.

We carried out two EUV outgassing studies (1) an investigation into outgassing potential vs. carboxylate structure, (2) a deuterium labeling study identifying where hydrogen is abstracted to create benzene and phenol.

2.2. Study 1: reaction monitoring via outgassed products

Previous MORE work has shown that variation in carboxylate structure results in significant changes in sensitivity, SEM stability and dissolution rate [10]. In order to test the effect of carboxylate structure on the degree of outgassing of CO$_2$, benzene and phenol, we synthesized a series of molecules of the general form Ph$_3$Sb(O$_2$CR')$_2$ (Fig. 4). The specific variation in this series of resists is increasing substitution of the carbon alpha to the carbonyl.

A series of side-by-side exposures revealed that for all three primary species, the amount of outgassing per photon varies significantly depending on the identity of R' as shown for CO$_2$ (Fig. 5). A two order-of-magnitude increase in CO$_2$ production was observed between Ph$_3$Sb(O$_2$CC$_6$H$_5$)$_2$ (MM-10) and Ph$_3$Sb(O$_2$CCH$_2$C$_6$H$_5$)$_2$ (MM-60). A strong correlation was found between the degree of outgassing (interpolated at a dose of 15 mJ/cm$^2$) and decarboxylation activation energy.

Decarboxylation is the breaking of the antimony-oxygen bond resulting in the loss of the carboxylate ligand which decomposes into CO$_2$ and R'. This process occurs post-photoionization due to photon or high energy electron interaction (Fig. 6). The decarboxylation activation energies used in this study were calculated for each unique antimony compound (Table 1).
Fig. 4. A series of Phenyl₃SbCarboxylate₂ resists were synthesized of increasing substitution at the α carbon to determine if the degree of outgassing changes with respect to the structure of R′.

Fig. 5. A plot of CO₂ outgassing for a series of antimony carboxylate resists illustrating the difference in reaction potential as a function of carboxylate ligand structure.

Fig. 6. The process of decarboxylation in an antimony carboxylate resist due to photon/electron interaction.

A decrease in the activation energy of decarboxylation correlates to an increase in outgassing rate for CO₂, benzene and phenol (Fig. 7 A and B). Upon further examination, it was observed that MM-49 is a significant outlier across all three primary outgassing species as illustrated in Fig. 7 in which the R² value was calculated with and without MM-49. As shown, the correlation between outgassing potential and energy of decarboxylation improved significantly upon omission of this particular resist. Further work is required to understand the unexpected reactivity of the isobutyrate ligand.

Fig. 7. A trend is observed for (A) CO₂ outgassing and (B) benzene and phenol outgassing. In which, the energy required for decarboxylation decreases in conjunction with increased outgassing per unit dose for a series of carboxylate ligands.

The results of this study demonstrate that the three primary outgassed species are generated at rates determined by the structure of the carboxylate ligand. This further confirmed that the carboxylate ligand is of primary focus in a mechanism of photo-decomposition.

Table 1. Energy of decarboxylation values calculated from individually modelled Ph₃Sb(O₂CR′)₂ molecules.

<table>
<thead>
<tr>
<th>Resist I.D.</th>
<th>Resist Structure</th>
<th>Decarboxylation Activation Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM-60</td>
<td>(C₆H₅)₃Sb(O₂CCH₂C₆H₅)₂</td>
<td>17.5</td>
</tr>
<tr>
<td>MM-13</td>
<td>(C₆H₅)₃Sb(O₂C(CH₃)₃)₂</td>
<td>22.6</td>
</tr>
<tr>
<td>MM-49</td>
<td>(C₆H₅)₃Sb(O₂CCH(CH₃)₂)₂</td>
<td>28.6</td>
</tr>
<tr>
<td>MM-17</td>
<td>(C₆H₅)₃Sb(O₂CCH₂CH₃)₂</td>
<td>29.5</td>
</tr>
<tr>
<td>JP-18</td>
<td>(C₆H₅)₂Sb(O₂CCH₃)₂</td>
<td>30.9</td>
</tr>
<tr>
<td>MM-10</td>
<td>(C₆H₅)₂Sb(O₂CC₆H₅)₂</td>
<td>35.5</td>
</tr>
</tbody>
</table>
2.3. Study 2: deuterium labeling study – source of hydrogen

Mass spectrometry results showed the formation of benzene and phenol during exposure of a series of antimony carboxylates. The outgassing of both substituents as stable molecules requires the donation of hydrogen from a source within the film. The identification of the source of these hydrogens provides insight into the reaction mechanism. In order to differentiate between hydrogens on the R-group vs. the carboxylate, a deuterium labeling study was performed. A partially deuterated form of JP-18 was synthesized in which every hydrogen composing the acetate ligand was substituted for deuterium (Fig. 8). Direct comparison of d₆-JP-18 and JP-18 outgassing mass spectra can identify the origin of the hydrogens that are combined with phenyl or phenoxy to yield benzene or phenol.

![Fig. 8. Phenyl₃SbAcetate₂ (JP-18) possesses two types of ligands from which hydrogen may be abstracted. The phenyl ligand and the acetate ligand. To distinguish the two types of hydrogens during mass spectrometry measurements a version of JP-18 was synthesized in which all acetate hydrogens were replaced with deuterium atoms referred to as d₆-JP-18.](image)

Side-by-side outgassing experiments were performed of JP-18 and d₆-JP-18. The data obtained for the appropriate mass ranges were compared to identify any shifts in mass denoting the abstraction of a deuterium versus hydrogen to create benzene and/or phenol. The data is plotted as relative outgassing in which the largest peak is normalized to one and the surrounding peaks are scaled accordingly.

No significant amu shift in benzene outgassing was observed between the JP-18 and d₆-JP-18 mass spectra during EUV or 80 eV electron beam exposure (Fig. 9). With a minimum of 95% isotopic purity, we can deduce that hydrogen is not abstracted at the acetate ligand to produce benzene during exposure. This experiment confirmed that a deuterium was not abstracted when creating benzene and although the only other type of hydrogen atom in d₆-JP-18 is from the phenyl ligand the possibility resides that another source of hydrogen may also be present in the form of H₂O or solvent. Further experiments were conducted to identify the likelihood of H₂O as a source of protons in the film (Section 2D).

The mass spectra of JP-18 and d₆-JP-18 in the mass range of phenol’s parent peak were compared (Fig. 10). A shift of one amu is observed between JP-18 and d₆-JP-18 for the outgassing of phenol. With a minimum of 95% isotopic purity we conclude that a hydrogen is abstracted from the acetate ligand to generate phenol during EUV and e-beam exposure.

The results for both benzene and phenol generation were surprising on two accounts: (1) each fragment is created from hydrogen abstraction at differing locations, and (2) the high isotopic purity illustrated that each byproduct has a single reaction pathway by which majority of the reactions occur.

![Fig. 9. Comparison of benzene outgassing between JP-18 and d₆-JP-18 exposed to EUV photons and 80 eV electrons. Deuterium labeling confirms that the formation of benzene does not occur through abstraction of a hydrogen from the acetate ligand.](image)

![Fig. 10. Comparison of phenol outgassing between JP-18 and d₆-JP-18 exposed to EUV photons and 80 eV electrons. Deuterium labeling confirms that the formation of phenol predominantly occurs through abstraction of a hydrogen from the acetate ligand and not abstraction of a phenyl hydrogen.](image)
2.4. The role of water

The generation of benzene by a single reaction pathway is dependent on the abstraction of a hydrogen from a phenyl ligand within the film. The comparison of JP-18 and d6-JP-18 provided conclusive evidence that benzene formation does not occur via hydrogen abstraction at the acetate, and although the only other source of hydrogen within the resist molecule lays in the phenyl ligand it may not be the only additional source in the film.

As no additional components make up the resist formulation the only other possible sources of hydrogen within the film are trace quantities of 1,2-dichloroethane (DCE) and H2O. The standard spincoating solvent for our antimony carboxylate platform is DCE. Due to its volatility and the low pressures of the outgassing chamber (1E-7 torr) we expect that very little DCE remains within our resist films. Conversely, water has the potential to remain in resist films. DCE has a low water solubility of 0.86% by weight [20], but the large amount of surface area by volume of a resist film and the ability of H2O to hydrogen bond may result in H2O being a source of hydrogen within the film.

To determine the presence of water within the film and its ability to participate in the photomechanism, two additional outgassing experiments were performed (1) a comparison of synthetic routes with and without the inclusion of H2O, (2) incorporation of D2O as a formulation additive to monitor d1-benzene formation.

JP-18 and d6-JP-18 were synthesized by two routes: one which included the use of H2O2 (30 wt.% in H2O) (S1) and the second excluding H2O (S2) entirely. As a control, both resists, synthesized by each method, were evaluated side-by-side to identify any significant changes in outgassing signature for the mass ranges of benzene and phenol (Figure 11 A and B). The data is plotted as relative outgassing in which the largest peak is normalized to one and the surrounding peaks are scaled accordingly.

A comparison of both synthesis methods for the deuterated and non-deuterated complex showed good agreement asserting that the presence of H2O pre-formulation has no effect on outgassing. Additionally, this experiment provides further evidence to the previously discussed deuterium-labelling study in which it was found phenol is generated upon abstraction of a hydrogen from the acetate ligand and benzene is not.

Experiment 2 aimed to purposefully dope a resist film with D2O and observe benzene outgassing in JP-18. A peak at 79 amu would be indicative of H2O’s ability to participate as a site of hydrogen abstraction. As DCE has poor water solubility additional solvents were added to the resist formulation.

Each resist film was monitored by mass spectrometer in the range of 70–100 amu during EUV exposure. Analysis of the compiled data confirmed that none of the formulations regardless of solvent or weight percent of D2O generated a peak of 79 or for that matter of 95 as would be expected if a deuterium atom were abstracted to create benzene or phenol. Additionally, a mass range of 15-25 amu was observed during pump down of the chamber, and upon EUV exposure of each film. No D2O was found leaving the film due to vacuum or exposure.

From these experiments, we conclude that water is not a significant source of hydrogen in our system and does not participate in the generation of benzene.

2.5. Mechanistic interpretation

Mechanistic interpretation is needed to understand the pathways by which reactions occur and thereby leave a nonvolatile photoproduct. Therefore, we drew from the well-established
Eight fundamental reactions are known to describe photons and electrons interacting with matter. Of the eight reactions, three are of primary focus for our resist system. The remaining five are either incompatible with thin film EUV chemistry or are subsequent processes of the three reactions of note. Utilizing a basic AB representation for our antimony carboxylate compounds and the simplifying assumption that A is electro-positive and B is electro-negative, we determine the following equations (Eqs. 1-3).

**Hole-Induced Reaction**

\[ hν + AB \rightarrow AB^+ + e^- \rightarrow A^+ + B^- \]  

(1)

**Dissociative Electron Attachment**

\[ e^- + AB \rightarrow A^- + B^- \]  

(2)

**Internal Excitation**

\[ e^- + AB \rightarrow A^- + B^- + e^- \]  

(3)

Substitution of the simplistic AB theme for \(R_3\text{SbX}_2\) illustrates the potential for six different reactive intermediates (Fig. 12).

\[ R^- \quad R_2\text{SbX}^- \quad R_2\text{SbX}_2^- \quad R_3\text{SbX}^- \quad \text{X}^- \quad \text{X}^- \]

Fig. 12. Potential reactive intermediates created during exposure based on examination of three fundamental photon/electron interactions with matter. Focus will be set toward radical intermediates.

From previous work [7,10,12] and the outgassing results described here, the predominant mechanism of EUV photodecomposition of these and related MORE compounds appear to involve rate limiting decomposition of the carboxylate ligands. We consider three mechanistic pathways each beginning with the cleavage of a different bond (Fig. 13). Pathway (1) involves the cleavage of the antimony-oxygen bond. Pathway (2) involves the cleavage of the \(R'\)-carbonyl bond, and lastly pathway (3) involves the cleavage of the oxygen-carbonyl bond. The first study, reaction monitoring via outgassed products, identified a strong correlation between the outgassing of \(\text{CO}_2\), benzene and phenol and the activation energy of decarboxylation for a series of carboxylate ligands. Based on this result, we propose that pathway 1 is the most probable mechanism of photodecomposition. Reaction pathways 1 and 2 result in intermediate complex \(B\) and may be the rate limiting transition step in the photomechanism.

Fig. 13. Schematic of proposed cleavage sites in antimony carboxylate molecules upon exposure to electrons or EUV photons, and subsequent decomposition pathways to produce \(\text{CO}_2\) and \(\text{CO}\). Results of outgassing experiments provide evidence that cleavage at site 1 is most probable and formation of reactive complex \(B\) may be the rate limiting transition step in the photomechanism.

Cleavage of the \(R'\)-carbonyl bond and the generation of \(\text{CO}_2\) results in reactive intermediate \(B\), a possible pathway to generate benzene. Additionally, reaction pathways 2 and 3, could result in the creation of intermediate \(C\), with the potential to generate phenol, via cleavage of the oxygen-carbonyl bond. The determination of benzene and phenol production will provide insight into the photoproduct left in the film.

Investigation into a potential pathway for benzene generation continued from reactive complex \(B\), where two pathways were explored (Fig. 14). In the upper pathway, complex \(B\) undergoes intramolecular hydrogen abstraction from the carboxylate, resulting in an antimony hydride which through reductive elimination produces benzene and an antimony oxide. Yet, from the deuterium labeling study we know that benzene does not abstract a hydrogen from the carboxylate, and thus we rule this out as a potential reaction pathway.
In a second potential pathway (Fig. 14), complex $B$ interacts with a neighboring $\text{Ph}_3\text{Sb}(\text{O}_2\text{CR}')_2$ molecule from which a hydrogen is abstracted from the phenyl ring, producing an antimony hydride. This hydride molecule can then reductively eliminate benzene in a way that satisfies our deuterium labeling study, leaving a three-coordinate antimony molecule in the film. Additionally, a new antimony species, with a cation on the phenyl ligand, is produced. This additional reactive site is not investigated here and is a focus for future work.

Two pathways by which complex $C$ could react to produce phenol were explored (Fig. 15). In the upper pathway, complex $C$ undergoes intramolecular hydrogen abstraction to form an antimony hydroxide from a carboxylate hydrogen. The radical carboxylate would decompose to form a ketene and an oxygen radical bonded to antimony like that of complex $C$. The antimony hydroxide complex could reductively eliminate to form phenol in accordance with the deuterium labeling results.

The second potential pathway to create phenol, similar to benzene, requires a neighboring $\text{R}_2\text{Sb}(\text{O}_2\text{CR}')_2$ molecule to interact with the reactive intermediate in question. Here, a hydrogen is abstracted from the carboxylate ligand of the neighboring molecule to form an antimony hydroxide which reductively eliminates to form phenol and a three-coordinate antimony complex. Again, a new reactive intermediate is formed due to hydrogen abstraction from the carboxylate. Further testing is required to propose how subsequent intermediates will play a role in the overall photomechanism.

The three-coordinate antimony compound, $\text{R}_2\text{SbO}_2\text{CR}'$, created alongside benzene and phenol may be a stable photoproduct and less soluble than the original five-coordinate antimony resist. Outgassing experiments have provided information regarding what leaves the film, and mechanistic interpretation has yielded predictions for potential stable photoproducts that can be targeted in future thin-film composition experiments.

3. Conclusions

The MORE platform investigates the potential of various metals across the periodic table for use in EUV photoresists. The antimony carboxylate resist system has shown good performance with the potential for moderate resolution at very low
exposure doses. To better understand and improve the capabilities of this resist system, the underlying mechanism(s) occurring during exposure must be understood.

We conducted outgassing experiments to investigate the mechanism of photodecomposition. Two studies were performed with non-polymerizable antimony compounds. The first study, reaction monitoring via outgassed products, revealed strong correlations between increased outgassing and decarboxylation activation energy (Figs. 5-7). In the second study, a deuterium-labeling experiment was conducted in which we tracked where a hydrogen was abstracted within the film to produce benzene and phenol. The results showed that benzene and phenol each abstract a hydrogen from separate ligands and do so with greater than 95% isotopic purity (Figs. 9-11). Additionally, we demonstrated that it is unlikely for H₂O in the film to play a significant role in the formation of benzene. The results of these studies were used in conjunction with literature on photon and electron interactions with matter in the gas phase to propose multiple reaction pathways to generate our three major outgassing byproducts and a possible photoproduct.

This work has expanded our view of EUV interactions with metal-containing resists and provided a path by which we can expand our knowledge of an antimony carboxylate photomechanism. Further work is required to validate a mechanism, but this research has demonstrated that techniques like in situ mass spectrometry during outgassing have the potential to provide significant insight to achieve that goal.

4. Experimental Methods

4.1. General

All reactions were carried out under a nitrogen atmosphere. All reagents including triphenylantimony(III), acetic acid, d₄-acetic acid were purchased from Sigma Aldrich. Triphenylantimony dichloride was synthesized through the previously published route [10]. All reagents were used as received unless otherwise specified.

4.2. General resist formulation and sample preparation

Resist formulations were made by dissolving solids in 1,2-dichloroethane and filtering through a 0.2 μm PTFE filter. Formulations were then spincoated onto 4-inch silicon wafers, precoated with an adhesion-promoting film (crosslinked hydroxyethyl methacrylate/methyl methacrylate copolymers).

4.3. Resist formulation preparation incorporating D₂O into sample film

A series of master batches were created of 20% by weight D₂O in a variety of solvents which were then used in the formulation of JP-18 at varying ratios to DCE (Table 2). The amount of D₂O in the formulation varied from 1–4 % by weight. After spincoating each film was exposed to EUV and compared to a standard coat of JP-18 formulated in DCE with no addition of D₂O or H₂O.

4.4. Computational methods for decarboxylation energy calculation

All quantum chemical calculations were performed using NWChem [22], and they were carried out in the following manner: Energies for all species were calculated in two stages with density functional theory. Each molecular structure was relaxed using the M06 functional [23] with the Hay and Wadt double zeta basis set, LANL2DZ and the LANL2DZ effective core potential for antimony atoms [24,25]. After structural relaxation, vibrational modes were computed with the same basis set by the method of finite differences, and thermochemical values were extracted from the vibrational data. More accurate self-consistent field energies for each structure were computed using the M06 functional with the Pople 6-311++G(3df,3pd) basis for C, H, and O [26], the 6-311G** basis for I, and the Def2-TZVP basis for antimony [27].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Formulation (DCE:Solvent)</th>
<th>Total wt.% D₂O</th>
</tr>
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<tbody>
<tr>
<td>Acetonitrile</td>
<td>4:1</td>
<td>4%</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>1,2-Dimethoxyethane</td>
<td>9:1</td>
<td>2%</td>
</tr>
<tr>
<td>Diglyme</td>
<td>19:1</td>
<td>1%</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>9:1</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>19:1</td>
<td>1%</td>
</tr>
<tr>
<td>1,2-Dimethoxyethane</td>
<td>9:1</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>19:1</td>
<td>1%</td>
</tr>
</tbody>
</table>

Bond dissociation energies were computed by taking the free energy difference of the fragments
Expected to significantly impact the overall free radicals and the energies of solvation were not model was not utilized because all species are rotational and translational entropies. A solvent were adapted from Grzeskowiak et al [28].

Gibbs free energies were computed according to:

\[ G = E_{ecf} + E_{zpe} + H_{corr} - T(S_{vib} + S_{trans} + S_{rot}) \]  \( (4) \)

Where \( E_{ecf} \) is the self-consistent field energy, \( E_{zpe} \) is the zero-point vibrational energy, \( H_{corr} \) is the thermal correction to the enthalpy as defined by NWChem, and \( S_{vib}, S_{rot}, \) and \( S_{trans} \) are the vibrational rotational and translational entropies. A solvent model was not utilized because all species are radicals and the energies of solvation were not expected to significantly impact the overall free energies.

4.5. Instrumentation and experimentation

Outgassing mass spectrometry experiments were adapted from Grzeskowiak et al [28]. E-beam exposures were carried out in a manner described exactly by this work. For EUV exposures, there was a lack of sufficient instrumentation to carry out quantitative EUV outgassing mass spectrometry for CO\(_2\), benzene and phenol with data reported in molecules per incident photon. In this case, the representative compound JP-18 was used as a benchmark.

Four to five coated wafers were loaded per vacuum cycle into a vacuum chamber capable of EUV exposure with an EQ-10M lab-scale EUV source. One wafer without resist (only adhesion promoting film) and one wafer of unexposed JP-18 were tested in every vacuum cycle (sample loading, pump down to vacuum, exposure, vent to atmosphere). Exposure of the wafer without resist (the “blank”) provided background data for every resist tested; exposure of JP-18 provided a normalization benchmark for every other compound to account for cycle-to-cycle variation in vacuum pressure and mass spectrometer sensitivity.

The other two to three wafers loaded in each vacuum cycle spanned the other compounds discussed in this paper. The vacuum pressure was allowed to stabilize while each sample was rotated to find unexposed material for the next exposure. Then the source power was measured again and the data collection mode was disengaged when switching to another loaded sample.

The mass spectrometer collected data in the 42-46 amu range to measure CO\(_2\) outgassing, and in the 70-100 amu range to measure both benzene and phenol outgassing. The area under the mass spectral chromatogram was integrated separately for each pulse, including for the “blank” exposure. The data for all exposures is processed, and then divided by the JP-18 30s exposure from that compound’s vacuum cycle. This normalized data is presented in Figs. 5-7. Similar exposures were carried out for d\(_6\)-JP-18 and non-deuterated JP-18 comparison.

4.6. Synthetic procedure for JP-18 – Ph\(_3\)Sb(O\(_2\)CCH\(_3\))\(_2\)

Triphenylantimony(V) diacetate was synthesized from a modified procedure by (Gushchin) [29]. Triphenylantimony(III) (3.53 g, 10 mmol) was dissolved in a 1:7 mixture of diethyl ether and 2-propanol. Acetic acid (1.8 g, 30 mmol) was added to the solution and the flask cooled to -15 °C and then hydrogen peroxide (1.1 mL, 10.5 mmol) was added dropwise over 5 minutes. Immediately upon addition of the H\(_2\)O\(_2\) a thick precipitate formed in the reaction vessel. This mixture was magnetically stirred for 3 hours and allowed to equilibrate to room temperature. The reaction was filtered through a medium frit and the solid washed with 2-propanol. The residue was crystallized from 10:1 chloroform:hexanes forming crystals overnight under reduced temperature. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.06 \) to 7.90 (m, 6H), 7.53 to 7.40 (m, 9H), 1.80 (s, 6H). Melting point 215 °C.

d\(_6\)-JP-18 – Ph\(_3\)Sb(O\(_2\)CCD\(_3\))\(_2\) was synthesized by the procedure outlined for JP-18 with the substitution of d\(_4\)-acetic acid. \(^1\)H NMR confirmed the absence of a proton peak from the acetate ligand. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.25 \) to 7.81 (m, 6H), 7.60 to 7.36 (m, 9H), 1.85 to 1.75 (s, 6H). Melting point 216 °C.

4.7. Synthetic procedure for triphenylantimony dicarboxylates – Ph\(_3\)Sb(O\(_2\)CR)\(_2\))

Triphenylantimony(III) (2.0 g, 4.7 mmol) was dissolved in dichloromethane (25 mL) in a 100 mL round-bottom flask equipped with a stir-bar. The appropriate potassium carboxylate salt (2 eq., 14.1 mmol) was added to the solution and the reaction was stirred under nitrogen for 16 hours. The
reaction mixture was filtered through a frit and the residual solid washed with 50 mL of DCM. The filtrate and washings were collected and the solvent removed under reduced pressure by rotary evaporation. Dependent on purity established by $^1$H NMR and DSC the product was crystallized overnight from ethyl acetate at -28 °C.

Acknowledgements

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