Isotopic Labeling Studies of EUV Photoresists Containing Antimony

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We have investigated the mechanism of photodecomposition of antimony carboxylate complexes of the type Ph₃Sb(O₂CR)₂ by means of EUV outgassing in combination with isotopic labeling. When exposed to EUV light, these compounds decompose to form CO₂, benzene and phenol. The source of hydrogen needed to create phenol can be traced to hydrogens originating in the original organometallic complex. However, it is much more difficult to trace the origin of the hydrogen needed to convert the phenyl groups to benzene (Ph-H). We propose that the primary source of hydrogen to create benzene is external to the film. Additionally, we have prepared isotopically-labeled versions of Ph₃Sb(O₂CCH(CH₃)₂)₂ in which the hydrogens in the isobutyrate ligand were replaced with 0, 1, 6 and 7 deuteriums, to provide information about the relative reactivity of these protons during EUV exposure as analyzed by mass spectrometry. High reaction selectivity was identified within the carboxylate dictated by hydrogen location relative to the carbonyl for both benzene and phenol generation. Lastly, the results of these studies were used to propose a series of reaction pathways to generate the aforementioned reaction byproducts.

Keywords: EUV, Photoresist, MORE, Mechanism, Antimony, Isotopic labeling

1. Introduction

Today, as extreme ultraviolet (EUV) lithography approaches integration into high volume manufacturing, photoresist performance remains a key challenge [1,2]. Several novel photoresist platforms have emerged in recent years in an attempt to optimize photon absorption and simultaneously improve resolution, line width roughness, and sensitivity [3-5]. One approach that has garnered significant attention is that of metal-containing photoresists. These systems utilize metals with higher EUV absorption coefficients compared to standard CAMP resists [6]. Inpria has demonstrated excellent lithographic performance and manufacturability of their tin-based photoresist [7,8]. The Ober group has demonstrated zirconium and hafnium nanoparticle photoresists capable of high resolution and improved etch resistance [9]. Additionally, our group has explored and evaluated resists composed of metals including cobalt, platinum, tin, antimony and bismuth [10-15].

Recently, the focus of our group has changed from the development of new resist platforms to the investigation of EUV photomechanisms. A number of papers have been published that explore the photomechanism through instrumentation such as XPS, FTIR, TGA, electrospray ionization mass spectrometry and modelling [16-20]. Our recent work has focused on investigating the photomechanism of our antimony-carboxylate platform, by studying the volatile photoproducts following exposure to EUV (Fig. 1) [21-23].

Here, we present two isotopic-labeling studies of antimony-containing EUV photoresists: (1) a comparison of isotopic composition of benzene and phenol generated during EUV exposure of Ph₃Sb(O₂CCH₃)₂ and Ph₃Sb(O₂CCH(CH₃)₂); and (2) a search for the source of hydrogen required to form benzene during EUV exposure. Additionally,
based on these isotopic labeling studies, we propose several mechanistic pathways leading to the formation of CO₂, benzene and phenol.

Fig. 1. (A) General schematic of pentacoordinate antimony carboxylate resists (B) a representative molecule of the antimony carboxylate platform, Phenyl₃Sb(O₂CCHCH₂)₂ (JP-20).

2. Experimental

2.1. General

All reactions were carried out under a nitrogen atmosphere and yellow light. Triphenylantimony(III), acetic acid, d₄-acetic acid, 1,2-dichloroethane, d₄-1,2-dichloroethane, d₆-acetone, anhydrous tetrahydrofuran, sodium borohydride and sodium borodeuteride were purchased from Sigma Aldrich. d₅-bromobenzene was purchased from Alfa Aesar. All reagents were used as received unless otherwise specified. Melting points were recorded on a DSC 200 F3 Maia® differential scanning calorimeter. ¹H-NMR spectra were recorded on a 400 MHz Bruker spectrometer.

2.2. General resist formulation and sample preparation

Resist formulations were prepared by dissolving solids in 1,2-dichloroethane and filtering through 0.45 μm PTFE filters. Two weight percent formulations were then spincoated onto 4-inch silicon wafers, precoated with an adhesion-promoting film (crosslinked hydroxyethyl methacrylate/methyl methacrylate copolymers).

2.3. Resist formulations incorporating D₂O

Three water miscible solvents, acetonitrile, 1,4-dioxane and 1,2-dimethoxyethane, were separately diluted with 20% by weight D₂O. Each mixture was used in the formulation of JP-18 with a 4:1 ratio of DCE to the D₂O miscible solvent resulting in a D₂O concentration of 4 weight percent. Each formulation was spincoated using standard conditions and evaluated by outgassing against a standard formulation of JP-18.

2.4. Instrumentation and experimentation

Outgassing mass spectrometry experiments were adapted from Grzeskowiak et al [24]. Mass spectral data was collected using a Pfeiffer PrismaPlus quadrupole mass spectrometer using positive ion detection. 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, the “blank”) was tested in every vacuum cycle (sample loading, pump down to vacuum, exposure, vent to atmosphere) providing background data for every resist tested.

The other four wafers loaded in each vacuum cycle spanned the antimony-carboxylate compounds discussed in this paper. The vacuum pressure was allowed to stabilize at ~10⁻⁷ Torr before exposures began. The EQ-10M EUV source power was measured before and after each compound was exposed to give accurate exposure dose information for the data shown in Sections 3.1 – 3.3 (Figs. 2, 4-8, see below). After source power measurements, the data collection mode of the mass spectrometer was engaged and the “blank” was exposed to EUV. Following exposure, data was collected for an additional two minutes as the outgassing signal decayed to unexposed background levels. At this point, a particular photoresist was exposed to EUV for the same amount of time as the “blank” wafer, and immediately followed by a two-minute period in which the decaying outgassing signal of low diffusivity molecules was collected. Every wafer was exposed for a series of three durations of 90 s, 180 s and 300 s at an average flux of 0.12 mW/cm². After all three exposure doses the source power was measured again before moving to another loaded sample.

The mass spectrometer collected data in the 30-120 amu range to measure the outgassing of known major outgassing species such as CO₂, benzene and phenol. Mass spectral data was not collected below 30 amu in order to maintain the sensitivity of the mass spectrometer to species with minimal outgassing signal. 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, with the corresponding “blank” exposure subtracted from the photoresist. This normalized data is presented in Figs. 2, 4-8.

2.5. Synthesis of 2-deuterio-2-propanol –
The synthesis of d1-isopropanol was adapted from a published procedure [25]. Sodium borodeuteride (1.0 g, 23.9 mmol) was dissolved in 30 mL of 0.1 M NaOH in a 100-mL round-bottom flask at 0 °C. Acetone (7-mL, 94.7 mmol) was added dropwise to the solution, maintaining a reaction temperature below 15 °C. After addition the reaction was left to stir one hour at reduced temperature. Then 5 M sulfuric acid was added until a pH of two was reached. The product was isolated by distillation (b.p. 79 °C). 1,1,1,3,3,3-Hexadeutero-2-propanol ((CD3)2CHOH) was synthesized by the procedure outlined for 2-propanol with the substitution of d6-acetone and sodium borohydride.

2.6. Synthesis of 2-Deuterio-2-bromopropane – ((CH3)2CDBr)

The synthesis was adapted from a published procedure [26]. To a stirring solution of d1-isopropanol (4.6 g, 75.3 mmol) cooled to -15 °C was added phosphorus tribromide (4.7-mL, 50.2 mmol) dropwise. The resulting solution was stirred overnight at room temperature. The product was isolated by distillation, the fraction distilling off at 58 °C. The product was redistilled and its purity checked by 1H-NMR. d6-2-bromopropane followed the same procedure.

2.7. Synthesis of 2-Deuterio-Isobutyric acid – ((CH3)2CDCOOH)

Magnesium turning (1.0 g, 41.2 mmol) in a 2-neck 100-mL round-bottom flask with reflux condenser and vacuum adapter were dried as described in the synthesis of d2-isobutyric acid. 45-mL tetrahydrofuran was added to the reaction vessel and the reaction heated to reflux. While heating 1,2-dibromoethane (0.35-mL, 4 mmol) was added via syringe. D5-bromobenzene (10 g, 61.7 mmol) solubilized in 17-mL tetrahydrofuran was added dropwise and the reaction stirred for 2 hours before removing the solvent by rotary evaporation. The residue was solubilized in ethyl acetate and filtered before evaporating the solvent leaving the crude product as a clear oil. The crude product was solubilized in diethyl ether and filtered. The product crystallized upon removal of diethyl ether by evaporation. Purity confirmed by 1H-NMR and DSC. Melting point 52 °C.

2.8. Synthesis of d15-triphenylantimony(III) – (C6D5)3Sb

Magnesium turning (2.25 g, 92.6 mmol) in a 2-neck 250-mL round-bottom flask with reflux condenser and vacuum adapter were dried as described in the synthesis of d2-isobutyric acid. 45-mL tetrahydrofuran was added to the reaction vessel and the reaction heated to reflux. While heating 1,2-dibromoethane (0.35-mL, 4 mmol) was added via syringe. 1,2-dibromoethane (0.35-mL, 4 mmol) was added via syringe. D5-bromobenzene (10 g, 61.7 mmol) solubilized in 17-mL tetrahydrofuran was added dropwise and the reaction stirred for 2 hours before removing the solvent by rotary evaporation. The residue was solubilized in ethyl acetate and filtered before evaporating the solvent leaving the crude product as a clear oil. The crude product was solubilized in diethyl ether and filtered. The product crystallized upon removal of diethyl ether by evaporation. Purity confirmed by 1H-NMR and DSC. Melting point 52 °C.

2.9. Synthesis of JP-18 – Ph3Sb(O2CCH3)2

Triphenylantimony (V) diacetate was synthesized from a modified procedure by (Gushchin) [27]. Triphenylantimony(III) (3.53 g, 10 mmol) was dissolved in a 1:7 mixture of diethyl ether and 2-propanol under magnetic stirring. Acetic acid (1.8 g, 30 mmol) was added to the solution and the flask cooled to -15 °C followed by dropwise addition of hydrogen peroxide (1.1 mL, 10.5 mmol) over five minutes. Immediately upon addition a precipitate formed in the reaction vessel. The mixture was stirred for three hours at room temperature. The precipitate was collected and washed with 2-propanol. The residue was crystallized from 10:1 chloroform:hexanes forming crystals overnight at -28 °C. 1H NMR (400 MHz, CDCl3) δ 8.06 to 7.90 (m, 6H), 7.53 to 7.40 (m, 9H), 1.85 to 1.75 (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_{6}-acetic acid. ¹H NMR confirmed the absence of a proton peak from the acetate ligand. Melting point 216 °C.

d_{21}-JP-18 – (C_{6}D_{5})_{3}Sb(O_{2}CCD_{3})_{2} was synthesized by the procedure outlined for JP-18 with the substitution of d_{4}-acetic acid and d_{15}-triphenylantimony(III). ¹H NMR confirmed the isotopic purity to be ~98% by comparison of integration values to a measured addition of 1,4-dioxane. Melting point 219 °C.

2.10. Synthesis of MM-49 – Ph_{3}Sb(O_{2}CCH(CH_{3})_{2})_{2}

Triphenylantimony (V) diisobutyrate was synthesized by the same general scheme as JP-18. Triphenylantimony(III) (3.53 g, 10 mmol) was dissolved in a 1:3 mixture of diethyl ether and 2-propanol. Isobutyric acid (2.64 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 five minutes. The reaction was magnetically stirred for sixteen hours at room temperature. The solvent was removed by evaporation under reduced pressure resulting in a clear oil which solidified on standing. Hexanes was added to remove soluble impurities and the reaction filtered. The residue was crystallized from ethyl acetate forming crystals at -28 °C. ¹H NMR (400 MHz, CDCl_{3}) δ 8.05 to 7.91 (m, 6H), 7.50 to 7.40 (m, 9H), 2.37 to 2.21 (m, 2H), 0.95 to 0.81 (d, 12H).

d_{2}-MM-49 – Ph_{3}Sb(O_{2}CCCH(CH_{3})_{2})_{2} was synthesized by the procedure outlined for MM-49 with the substitution of d_{1}-isobutyric acid. ¹H NMR confirmed the absence of a β hydrogen peak.

d_{12}-MM-49 – Ph_{3}Sb(O_{2}CCH(CD_{3})_{2})_{2} was synthesized by the procedure outlined for MM-49 with the substitution of d_{6}-isobutyric acid. ¹H NMR confirmed the absence of a α hydrogen peak.

3. Results and discussion

3.1. Study 1: benzene and phenol formation – carboxylate reactivity

3.1.1. Acetate Ligand – Ph_{3}Sb(O_{2}CCH_{3})_{2}

Previously, we found that EUV exposure of antimony carboxylate resists produce CO_{2}, benzene and phenol as the primary volatile photoproducts [21]. We used isotopic labeling of the acetate ligand in Ph_{3}Sb(O_{2}CCH_{3})_{2} (JP-18) to trace the origin of the hydrogens required to convert the phenyl ligand to benzene or phenol (Fig. 2A).

Side-by-side EUV exposures of d_{0}-JP-18 and d_{6}-JP-18 demonstrated marked different pathways for the formation of benzene and phenol. Mass spectral data showed that < 5% of the hydrogen used to make benzene came from the acetate ligand (Fig. 2B). Whereas, > 95% of the hydrogen used to make phenol came from the acetate ligand (Fig. 2C). Additional experiments were conducted to determine the hydrogen source(s) to create benzene.

3.1.2. Isobutyrate Ligand – Ph_{3}Sb(O_{2}CCH(CH_{3})_{2})_{2}

In a previous study, we showed that compounds of the type Ph_{3}Sb(O_{2}CR')_{2} exhibited EUV reactivity that was well-correlated with the strength of the carbonyl-R' bond [21]. The compound Ph_{3}Sb(O_{2}CCH(CH_{3})_{2})_{2} (MM-49), however, was found to be much more reactive than could be predicted by its carbonyl-R' bond.

Fig. 2. Initial isotopic labeling experiment utilizing EUV outgassing to determine the source of hydrogen abstraction to create benzene and phenol during exposure of Phenyl_{3}Sb(O_{2}CCH_{3})_{2} (JP-18) [21]. The data for each compound was normalized to the largest peak.
energy. Here, we use isotopic-labeling studies in an effort to discover the reasons behind the unanticipated reactivity of this ligand.

Three \( \text{Ph}_3\text{Sb}(\text{O}_2\text{CCH(CH}_3)\text{}_2)\) \((\text{MM}-49)\) molecules were synthesized with selectively deuterated carboxylic acid ligands (Fig. 3). The isotopic composition of benzene and phenol was used to determine the reactivity of the \( \alpha \) and \( \beta \) positions in the molecule. All compounds were evaluated side-by-side using EUV outgassing to follow the generation of benzene and phenol, and the results were compared to the established reactivity of the acetate ligand in the creation of said species.

Benzene production was evaluated by monitoring a mass range of 76–80 amu to evaluate the production of \( \text{d}_0 \)-benzene vs. \( \text{d}_1 \)-benzene, at 78 and 79 amu, respectively (Fig. 4). An increase in the production of \( \text{d}_1 \)-benzene is evident upon exposure of \( \text{d}_2 \)-\( \text{MM}-49 \) vs. \( \text{d}_0 \)-\( \text{MM}-49 \). We estimate that phenyl radicals obtain \(~30\%\) of their hydrogen atoms from the \( \alpha \)-position of \( \text{MM}-49 \). However, analysis of the isotopic composition of benzene upon exposure of the compound labeled in the \( \beta \)-position \( \text{d}_{12} \)-\( \text{MM}-49 \) produces only a small amount of \( \text{d}_1 \)-benzene. We estimate that phenyl radicals obtain \(~5\%\) of their hydrogen atoms from the \( \beta \)-position of \( \text{MM}-49 \). These results indicate that, unlike the acetate ligand, the isobutyrate ligand can react in the process to create benzene, but with a high degree of selectivity within the ligand.

The generation of phenol was assessed within the mass range of 93–97 amu for the exposures of \( \text{d}_0 \)-\( \text{MM}-49 \), \( \text{d}_2 \)-\( \text{MM}-49 \) and \( \text{d}_{12} \)-\( \text{MM}-49 \) (Fig. 5). The isotopic ratios of \( \text{d}_0 \)-phenol (94 amu) and \( \text{d}_1 \)-phenol (95 amu) were compared for each compound. The \( \alpha \)-deuterated complex, \( \text{d}_2 \)-\( \text{MM}-49 \), exhibited minimal reaction to create phenol. While the \( \beta \)-deuterated complex, \( \text{d}_{12} \)-\( \text{MM}-49 \), displayed significant reactivity in the creation of phenol calculated at approximately fifty six percent of total phenol generation.

Outgassing studies revealed that the \( \alpha \)- and \( \beta \)-hydrogens have complementary reactivities (Table 1). Furthermore, unlike \( \text{JP}-18 \) the production of phenol from \( \text{MM}-49 \) does not occur
through hydrogen abstraction from one majority source but multiple locations.

Table 1. Summary of hydrogen site reactivity of the acetate and isobutyrate carboxylate ligands with respect to benzene and phenol generation.

| Reactivity Ratio by Hydrogen Type | Acetate α | β |
|---------------------------------|-----------|---|
| Benzene                        | < 5%      | 31% 5% |
| Phenol                         | > 95%     | < 5% 56% |

3.2. Study 2: phenyl to benzene—source of hydrogen

Here, we describe a series of experiments to determine if phenyl radicals created during the photolysis of JP-18 acquire hydrogens from (1) the acetate ligand, (2) other phenyl groups on JP-18, (3) the spin-coating solvent, (4) our organic underlayer, or (5) water trapped in the film.

3.2.1. Acetate ligand

Last year, we described our initial experiments to trace the origin of the hydrogen that is needed to convert phenyl to benzene by exposing Ph₃Sb(O₂CC₃D₃)₂ and Ph₃Sb(O₂CCH₃)₂ to EUV light [21]. The isotopic composition of the resulting benzene clearly showed that benzene is created via a pathway in which hydrogen is taken from a source other than acetate. Less than five percent of the hydrogen comes from acetate.

3.2.2. Other phenyl groups

We synthesized a fully-deuterated version of JP-18 [Ph³Sb(O₂CCD₃)₂; d₂₁-JP-18] for this study. EUV exposure of resist films containing either d₀- or d₂₁-JP-18 produced mass spectra of the benzene products (Fig. 6). Comparison of the m/e values of 83 (d₂-benzene parent ion) and 84 (d₀-parent ion) shows that a small amount of deuterium is transferred from the phenyl groups on antimony to form d₂-benzene. At most, only ~15% of benzene is generated by this route. Therefore >80% of hydrogen is abstracted from outside of the antimony complex.

3.2.3. Organic underlayer

We prepared a coating of d₂₁-JP-18 onto underlayer and onto a clean wafer, exposed to EUV and evaluated the mass spectra of the resulting benzene molecules. There was very little difference between the two samples of benzene (Fig. 7A). Therefore, we conclude that the organic underlayer contributes less than five percent of total benzene.

3.2.4. Solvent

We prepared coatings of d₂₁-JP-18 using fully-deuterated and non-deuterated versions of our casting solvent, 1,2-dichloroethane (d₀-DCE and d₁-DCE). Coatings were exposed to EUV light and the mass spectra of the resulting benzene were compared (Fig. 7B). The two spectra are nearly identical. Therefore, we conclude the formulation solvent contributes less than five percent of hydrogen abstracted to create benzene.

3.2.5. Water

We incorporated D₂O into various formulations of d₀-JP-18, prepared coatings, exposed to EUV and evaluated the mass spectra for the production of d₁-benzene. Minimal
generation of d$_1$-benzene was observed. Thus, we conclude that water is not a significant source of hydrogen in our system and does not participate in the generation of benzene.

3.2.6. External sources of hydrogen

Our isotopic-labeling experiments indicated that ~20% of the phenyl radicals generated by EUV photolysis of JP-18 acquire hydrogen atoms from within the film. We, therefore, conclude that most phenyl radicals may acquire hydrogen atoms from sources outside of the resist film. Such external hydrogen sources could include water or other compounds adsorbed to the walls of the chamber.

3.2.7. Evidence that carboxyl radicals leave the resist film

The concept of reactive fragments leaving the film is supported by the detection of a carboxylate fragment in which the oxygen–carbonyl bond is cleaved during exposure and the fragment is identified by the mass spectrometer. An aryl-carbonyl was observed during the exposures of Ph$_3$Sb(O$_2$CC$_6$H$_5$)$_2$ (MM-10) and its deuterated carboxylate counterpart d$_{10}$-MM-10 at 105 and 110 amu, respectively (Fig. 8A). In addition, the alkyl-carbonyl fragment is present during the exposure of Ph$_3$Sb(O$_2$CCH(CH$_3$)$_2$)$_2$ (MM-49) and its partially deuterated counterpart d$_2$-MM-49 at peaks of 71 and 72 amu, respectively (Fig. 8B).

3.3. Mechanistic interpretation

The ultimate goal of this work is to propose a series of reaction pathways to describe the mechanism of photodecomposition. Interpretation of how benzene and phenol are generated during exposure provides answers to the process by which the nonvolatile photoproduct is formed.

Prior work investigating the EUV photomechanism of antimony-carboxylate resists revealed a correlation between the strength of the antimony-carboxylate bond, dependent on the identity of R', and the degree of outgassing of benzene, phenol and CO$_2$ [21]. Based on our isotopic labeling studies, we propose a reaction pathway to form benzene (Fig. 9). Initial bond cleavage occurs at the carboxylate in accordance with previous work resulting in the generation of CO$_2$ and R'. The loss of the carboxylate ligand results in an Sb(IV) complex which loses a phenyl radical to reduce to an antimony(III) photoproduct. Most of the phenyl radicals leave the film before they can be converted to benzene (Section 3.1).

We propose two reaction pathways to create phenol (Fig. 10). Pathway (2) undergoes initial bond cleavage of the oxygen–carbonyl bond resulting in a Ph$_3$(R'CO$_2$)Sb–O∙ radical and an alkyl carbonyl compound as described in Section 2.2. Pathway (3) initiates reaction through cleavage of the carbonyl–R' bond corresponding to the correlation to decarboxylation energy established in our previous work. Once the R' group is removed, the complex could generate CO$_2$ or CO, and if it’s the latter a Ph$_3$(R'CO$_2$)Sb–O∙ radical is formed like that of pathway (2). Currently, carbon monoxide is difficult to identify due to its overlap with N$_2$ as well as fragmentation.
Fig. 8. Outgassing spectrum of two antimony-carboxylate photoresists show evidence of reactive intermediates leaving the film by cleavage of the oxygen-carbonyl bond. Assignment of mass peaks corroborated by isotopically labeled carboxylate compounds. (A) Mass spectrum of Phenyl₃Sb(O₂CC₆H₅)₂ (MM-10) and d₁₀-MM-10 (B) Mass spectrum of Phenyl₃Sb(O₂CC(CH₃)₂)₂ (MM-49) and d₂-MM-49.

Fig. 9. A proposed reaction pathway to form benzene upon exposure of Ph₃Sb(O₂CR')₂ resists. Loss of a carboxylate and a phenyl ligand results in an antimony(III) photoproduct.

Fig. 10. Two proposed reaction pathways to form phenol during exposure of Ph₃Sb(O₂CR')₂ resists in which an antimony hydroxide intermediate is formed and undergoes reductive elimination to generate phenol and an Sb(III) photoproduct.

4. Conclusion
This paper describes several studies utilizing isotopic labeling in combination with EUV outgassing to determine the pathways by which
volatile photoproducts are created during exposure. This method provides information leading to a better understanding of EUV exposure mechanisms of metal-containing resists. Carboxylate reactivity was examined for acetate and isobutyrate ligands. Deuterium labeling of the acetate ligand showed that >95% of the phenol is created by abstraction of the acetate hydrogen. Deuterium labeling studies of the isobutyrate ligand provided information about the relative reactivity of the \( \alpha \)- and \( \beta \)-positions in the isobutyrate ligand in comparison to the reactivity of the \( \alpha \)-position in the acetate ligand (Table 1). A high degree of selectivity was shown between the two positions, and additional reaction pathways are proposed for both benzene and phenol.

Our second study used a fully-deuterated isomer of \( \text{Ph}_3\text{Sb(O}_2\text{CCH}_3)\_2 \) to track the source of hydrogens needed to convert phenyl radicals to benzene. By careful analysis of the isotopic purity of \( d_5 \)-benzene vs. \( d_6 \)-benzene, the phenyl ligand was revealed to act as a source of hydrogen for fifteen percent of benzene production. However, \( \sim 80 \% \) of hydrogen is unaccounted for after additional experiments provided evidence that ruled-out the underlayer, casting solvent and \( \text{H}_2\text{O} \) within the film as sources of hydrogen. Consequently, after testing every possible source of hydrogen within the film we infer that the hydrogen required to convert a phenyl radical to benzene may originate outside of the resist film, and within the vacuum chamber. Evidence of other radical species leaving the resist film were also presented.

A mechanism was proposed for the generation of benzene and phenol utilizing the accumulated results of the antimony-carboxylate resists studied. A common non-volatile antimony photoproduct was proposed as the result of benzene and phenol outgassing. Further study will concentrate on elucidating the composition of the antimony photoproduct, and its imaging mechanism to improve overall lithographic capabilities.

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