Polymerizable Olefins Groups in Antimony EUV Photoresists

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Many antimony-carboxylate complexes containing polymerizable olefins are highly sensitive EUV photoresists. Herein we report two approaches by which we explored the reactivity of polymerizable olefin antimony carboxylate photoresists to improve lithographic performance. First, we explored the effect of replacing three phenyl groups with methyl groups in an effort to increase the relative concentration of olefins vs. size of the molecule. Second, we explored the effect of increasing the number of polymerizable olefins from two to five. This approach examines the use of tris(4-vinylphenyl)antimony-dicarboxylate complexes as photoresists and the developer chemistry capable of patterning highly crosslinked substrates.

Key Words: EUV, Photoresist, Antimony, Carboxylate, Olefin, Crosslinked.

1. Introduction

To achieve the best possible resolution, line-edge roughness (LER) and sensitivity, many groups around the world are developing EUV photoresists containing elements in the periodic table that strongly absorb EUV light [1-15]. Our group has developed multiple organometallic resist platforms including metals such as platinum, palladium, cobalt, bismuth, antimony and tin [4-8]. We have developed palladium oxalates that exhibit positive-tone imaging, developed tin carboxylates that exhibit very low line-edge roughness, and developed antimony-carboxylates that exhibit excellent photospeed [4-8].

Two of the first antimony resists developed by our group were triphenylantimonydiacrylate (JP-20) and triphenylantimonybis(4-vinylbenzoate) (JP-30) [7]. Upon exposure to EUV light, JP-20 produces contrast curves with high photosensitivity and high contrast (Figure 1A). This resist also resolves negative-tone dense-line patterns down to 16-nm half-pitch at very low doses using either hexanes or water as developers (Figure 1B). Unfortunately, however, the dense-line patterns of JP-20 are very sensitive to SEM electrons (~1 keV) such that the dense lines evaporate after two scans. JP-30 is also a fairly sensitive photoresist, but it is not quite as sensitive as JP-20. It provides contrast curves exhibiting high speed and high contrast, and prints dense-line patterns with resolution down to 22 nm (Figure 2). Unlike JP-20, however, JP-30 is very stable in the SEM.

JP-20 and JP-30 demonstrate a performance trade-off. Both compounds contain two olefins, but vary greatly in molecular weight and carbon content. The smaller JP-20 is faster, but evaporates quickly in the SEM; the larger JP-30 is about three times slower, but is perfectly stable in the SEM. Additional work by our group demonstrated a strong correlation between the sensitivity of olefin-containing antimony resists and the relative concentrations of olefins in the compound, known as the Polymerizable Olefin Loading (POL) [7]. The POL value is equal to the number of polymerizable olefins in a molecule divided by the number of atoms excluding hydrogen.
In this paper, we explored the extremes of our sensitivity/POL correlation using two approaches. First, we increased the relative olefin concentration (POL) in the resists by replacing the three aromatic groups bound directly to antimony with methyl groups. Second, we increased the number of olefins from two to five (Figure 3).

2. Experimental

2.1. General

1. 2-dichloroethane, hexanes, toluene, propylene glycol monomethyl ether acetate, dichloromethane, 2-butanone and hexanoic acid were purchased from Sigma Aldrich and used without further purification. 0.26 N Tetramethylammonium hydroxide, water and 2-propanol were provided by the facility where the exposures were performed.

2.2. Photoresist Formulation & Coating

All photoresist films were formulated at 1.5-2 wt.% solids in 1,2-dichloroethane. Once solubilized the formulations were filtered through 0.45 μm PTFE filters and spincoated onto 4-inch silicon wafers, precoated with an adhesion-promoting film (crosslinked hydroxyethyl methacrylate/methyl methacrylate copolymers). The spin conditions were 2000 rpm for 45 seconds. No pre- or post-exposure bakes were performed unless specified.

2.3. Instruments

Film thicknesses were measured using a J. A. Woollam M-2000 fixed angle ellipsometer equipped with Complete Ease software. The thicknesses were fitted using a Cauchy model for the photoresist and underlayer. The dense line patterning exposures were characterized by a LEO 1550 SEM and a Zeiss Supra 55VP at 1–2 keV accelerating voltage using an in-lens detector.

2.4. PSI XIL-II EUV Interference Lithography Beamline

EUV exposures performed at the Paul Scherrer Institut XIL-II beamline. 13.5 nm light was generated by an undulator synchrotron source and illuminated the photoresist samples as a spatially-coherent beam of EUV light. Contrast curve samples were composed of twenty-five exposures.
3. Results and Discussion

3.1. \((\text{CH}_3)_3\text{Sb(O}_2\text{CR'})_2\) Photoresists

To increase the olefin concentration and the EUV optical density of our mononuclear antimony resists, we explored the possibility of replacing the phenyls in compounds such as \(\text{JP}-20\) and \(\text{JP}-30\) with smaller alkyl groups \(\text{R}\). Thus, we synthesized a series of \(\text{R}_2\text{Sb(O}_2\text{CR'})_2\) photoresists and lithographically evaluated each to observe their performance relative to \((\text{C}_6\text{H}_3)_3\text{Sb(O}_2\text{CR'})_2\) photoresists. The change from aromatic \(\text{R}\)-groups to alkyl groups such as methyl, ethyl and isopropyl resulted in \(\text{R}_2\text{Sb(O}_2\text{CR'})_2\) complexes that were nonvolatile as bulk solids but too volatile as thin films. \((\text{CH}_3)_3\text{Sb(O}_2\text{CR'})_2\) compounds where \(\text{R'} = -\text{CH}_3, -\text{C(CH}_3)_2, -\text{CHCH}_2\) or \(-\text{(CH}_2)_4\text{CH}_3\) all lost considerable film thicknesses at ambient pressure and almost instantaneously lost all film thickness under vacuum. The only way to compensate for this volatility problem was to use large carboxylate ligands such as benzoate or its derivatives. We found that trimethylantimononybis(4-vinylbenzoate) \((\text{JP}-36)\) can be coated into an amorphous film that does not evaporate under vacuum.

Trimethylantimononybis(4-vinylbenzoate) \((\text{JP}-36)\) has fifteen fewer carbon atoms than \(\text{JP}-30\) and based on our POL sensitivity correlation was predicted to have an \(E_{\text{max}} < 2 \text{ mJ/cm}^2\) \([6, 18]\). However, contrast curves of \(\text{JP}-36\) show the \(E_{\text{max}}\) (dose to achieve maximum thickness) to be about 40-50 mJ/cm\(^2\) (Figure 4A). This result is in direct contradiction to the POL correlation and points to an important role played by the aromatic groups that are bound directly to antimony in the EUV exposure mechanism.

The methyl \(\text{R}\)-groups improve dissolution selectivity over phenyl ligands. \(\text{JP}-36\) can be successfully developed in \(\text{H}_2\text{O}\), hexanes and PMA with all developments exhibiting similar contrast and minimal top-loss. \((\text{C}_6\text{H}_3)_3\text{Sb(O}_2\text{CR'})_2\) photoresists do not have similar performance when developed in hexanes vs. water, and most have no dissolution contrast in more aggressive organic solvents such as PMA. \(\text{JP}-36\) resolves patterns down to 30-nm half-pitch with minimum pattern collapse when developed for forty-five seconds in hexanes (Figure 4B). Characterization by SEM of \(\text{JP}-36\) had no pattern degradation even with the large reduction in carbon-content relative to \(\text{JP}-30\). This result further illustrates that the carboxylate ligand plays a significant role in the photoresists stability.

![Fig. 4. (A) Contrast curves of \(\text{JP}-36\) developed in various solvents. All three development conditions provide similar sensitivity and contrast unlike that seen for \((\text{C}_6\text{H}_3)_3\text{Sb(O}_2\text{CR'})_2\) photoresists. (B) Dense line patterning of \(\text{JP}-36\) developed in hexanes [17]. The dose to pattern does not follow the POL sensitivity trend suggesting the R-group composition plays a significant role in the FRP mechanism.](image)

3.2. Increasing Olefin Content

To explore the capability of resists with 3-5 olefins/molecule, we made molecules in which the phenyls that are bound to antimony are replaced by styrene \([15]\). A series of \((4-\text{C}_6\text{H}_4\text{-})_3\text{Sb(O}_2\text{CR'})_2\) photoresists were synthesized ranging in olefin content from three to five per molecule. Unfortunately, unexposed thin films of...
tristyreneantimony-dibenzoate (JP-41) and trisstyreneantimonydiacrylate (LD-1), with three and five olefins respectively, cannot be dissolved in water, hexanes or PMA after contrast-curve exposures (Figure 5). A wide range of organic and alcohol developers were tested on additional contrast-curve samples without success. Our hypothesis is that the increase in olefins allow for uncontrolled polymerization to occur into the unexposed regions of the film preventing dissolution in standard solvents.

Fig. 5. Photographs of contrast-curve samples for three resists. Dicarboxylate complexes (e.g. JP-20) upon development in hexanes solution fully develop away the unexposed regions. Tristyreneantimony-dicarboxylate complexes containing three–five olefins do not develop in hexanes solution presumably due to enhanced cross-linking interactions. More reactive developer solutions were required to successfully pattern these photoresists.

Reactive developers containing strong acid or base were used to successfully develop these high olefin-containing complexes. Reactive developers are well known in the IC industry with tetramethylammonium hydroxide (TMAH) being one of the most common developers [1]. In addition, previous work by our group has shown the potential for acidic developers to have dramatic changes on organometallic photoresist performance depending on the acid used [15].

The combination of highly crosslinked photoproduct and aggressive solvents provided the means to pattern dense lines down to 22-nm half-pitch with less line collapse and higher sensitivity than di-olefin photoresists (Figure 6). Fine-tuning of acid or base concentration, and the solvent may allow for even higher resolution patterning.

Fig. 6. A series of (C₈H₇)₃Sb(O₂CR')₂ photoresists and their lithographic capabilities upon development in reactive solvents [17]. Development conditions: For JP-41, JP-44; Dose: 8.2 mJ/cm²; 10% IPA in 0.26 N TMAH in 5 min with water rinse. For LD-1; Dose: 8.2 mJ/cm²; 10% hexanoic acid in hexanes for 45 s.

4. Conclusion

The incorporation of olefins into antimony complexes provides EUV resists with excellent photospeed. JP-20 (triphenylantimonydiacrylate) prints dense lines with sizing doses as low as 5-9 mJ/cm², but evaporated quickly when exposed to SEM electrons. JP-30 (triphenylantimonybis(4-vinylbenzoate)) is capable of resolving dense line patterns down to 22 nm half-pitch at moderate doses with no discernable pattern degradation during SEM characterization.

Here, we explored the limits of our POL correlation by (1) reducing the size of the ligands bound to antimony and by (2) creating antimony compounds with 3-5 olefins/molecule. We found that the replacement of phenyl groups with methyl groups produced photoresists that did not follow the sensitivity vs. olefin concentration (POL) correlation that we had established earlier. Instead, the trimethylantimony complexes were about 25 times slower than was expected. This result points to the importance of the role played by phenyl groups when bound directly to antimony in the EUV exposure mechanism.

We also found that resists prepared using three or more olefins were so fast that resist films that unexposed films could not be fully cleared using conventional developers. We found that these resist could provide good images with reactive developers were used.
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17. All SEM images show dense-line (line/space = 1:1) patterns. Line size is shown as h/p or half-pitch.
18. The Polymerizable Olefin Loading (POL) of (CH3)3Sb(C6H4CH=CH2)2 (JP-36) = 100% * 2 olefins / 26 non-hydrogen atoms = 7.7%. When compared to the POL plot in Ref 6, the predicted Emax is < 2 mJ/cm².