

Investigation of novel inorganic resists materials for EUV lithography

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ABSTRACT

Recently, both PSI¹ and ASML² illustrated champion EUVL resolution using slow, non-chemically amplified inorganic resists. However, the requirements for EUVL manufacturing require simultaneous delivery of high resolution, good sensitivity, and low line edge/width roughness (LER/LWR) on commercial grade hardware. As a result, we believe that new classes of materials should be explored and understood. This paper focuses on our efforts to assess metal oxide-based nanoparticles as novel EUV resists³. Various spectroscopic techniques were used to probe the patterning mechanism of these materials. EUV exposure data is presented to investigate the feasibility of employing inorganic materials as viable EUV resists.

Keywords: non-chemically amplifies photoresists, EUV photoresists

1. INTRODUCTION

Extreme Ultraviolet Lithography (EUVL) remains an attractive candidate for next generation patterning technologies. As the introduction of EUVL to high-volume manufacturing is pushed to smaller technology nodes, resist performance plays an increasingly important role in the overall development of EUV technology. Strict requirements for resolution, sensitivity and line width roughness (LWR) are imposed, presenting numerous challenges for resist manufacturers¹⁻³

Chemically amplified resists (CARs) have continually been exploited to meet the scaling requirements of the semiconductor industry. However, the extension of these systems to EUVL is met with a variety of roadblocks. CARs suffer from limiting resolution due to acid blur⁴. Sensitivity is limited due to a weak EUV power source and shot noise⁴. Because of these problems, it is necessary to explore novel resist chemistries and architectures that can overcome the limitations and extend EUV resists to future technology nodes. Inorganic-based resist systems are starting to gain traction in the photoresist community, as 8nm half-pitch line/space patterns have been demonstrated with a metal oxide-based material⁴. As this is both a novel structure and photochemistry that shows promise to extend beyond the capabilities of traditional CAR resists, it is necessary to gain a deeper understanding of this new class of materials.

Previously, Ober et. al. reported a novel inorganic/organic hybrid nanoparticle resist system capable of resolving 30 nm half-pitch features with high sensitivity of 5 mJ⁵. This is a promising system that can potentially address the issue of low sensitivity seen with inorganic-based systems while maintaining high resolution. This paper aims to provide an in-depth analysis of the resist structure to determine the main components responsible for lithographic performance. Spectroscopic studies have been employed to gain further insight into the patterning mechanism.

2. EXPERIMENTAL

2.1 Materials

All solvents and starting materials were purchased from Sigma Aldrich and used as received. The inorganic/organic hybrid nanoparticles were synthesized using a hydrolysis/condensation reaction highlighted in a previously published procedure⁵

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2.2 Measurements

Resist solutions were made by dissolving HfO₂-MAA/BZA and TPS-Nonflate PAG in PGMEA. ¹H NMR was performed using a Bruker AVANCE III 400 MHz NMR. FT-IR measurements were carried out using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. EUV exposures were performed using the LBNL EUV MET tool.

3. RESULTS AND DISCUSSION

This study was performed to investigate the key components of the nanoparticle structures that contribute to the resolution and sensitivity of the resist. Both the metal oxide core and the surrounding ligands were varied in an effort to identify the most significant contributor to the resist performance. A total of four resist structures were investigated, HfO₂-MAA/BZA, HfO₂-MAA/4VBA, ZrO₂-MAA/BZA and ZrO₂-MAA/4VBA, which are depicted in figure 1. The size of the particles, as well as the ligand ratios, was kept constant. The four resist systems were evaluated via EUV exposures, with SEM images of the exposures shown in figure 2.

There was little variation in both resolution and sensitivity between two metal cores, HfO₂ to ZrO₂, with the same surrounding ligands (figure 2a and 2c). Comparing HfO₂-MAA/BZA to ZrO₂-MAA/BZA, both resists resolved 28 nm, with comparable doses of 45 and 42 mJ, respectively. However, resists with the same core but different ligands had significant differences in both resolution and sensitivity (figure 2a and 2b). Comparing HfO₂-MAA/4VBA to HfO₂-MAA/BZA, the former resist showed extremely high sensitivity of 0.5 mJ, and resolution down to 50 nm half-pitch, while the latter resolved 28nm half pitch lines with a sensitivity of 45 mJ. It is evident that the key to nanoparticle resist design lies in the ligands surrounding the core, and not the metal inside the core.

The ratio of two different bound ligands is another variable that can affect resist performance. A set of three HfO₂-MAA/BZA nanoparticles were synthesized, each with different ratios of methacrylate to benzoate ligands. EUV contrast curves, shown in figure 3, highlight the effects of ligand ratio on EUV sensitivity. By increasing the amount of MAA ligand with respect to the BZA ligand, the sensitivity of the resist increases dramatically.

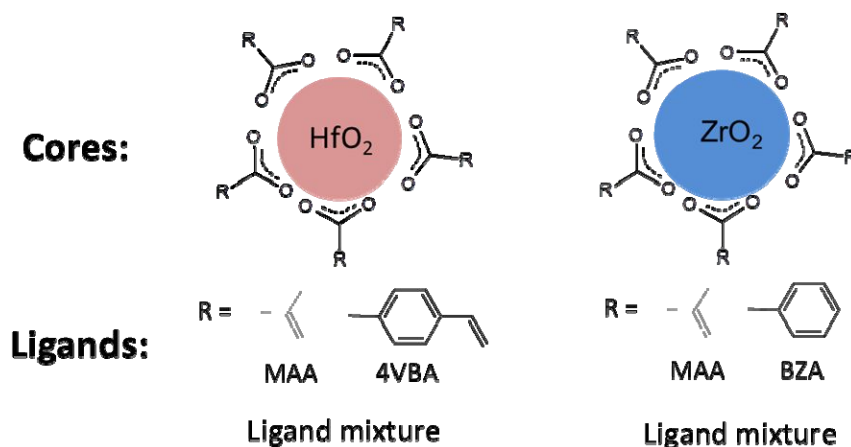


Figure 1. Structures of nanoparticle resists

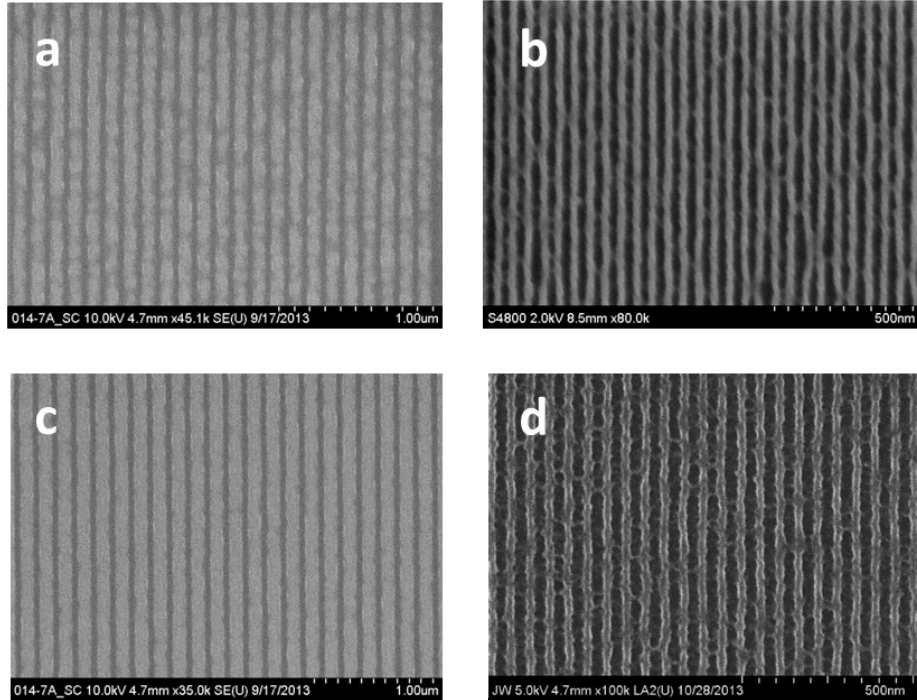


Figure 2. SEM images of nanoparticles resists: a) HfO_2 -MAA/4VBA, 0.5 mJ, 50 nm half pitch b) HfO_2 -MAA/BZA, 45 mJ, 28 nm half pitch, c) ZrO_2 -MAA/4VBA 0.5 mJ, 50 nm half-pitch and d) ZrO_2 -MAA/BZA, 42 mJ, 28 nm half pitch

EUV Contrast Curves MAA : BZA Ratio

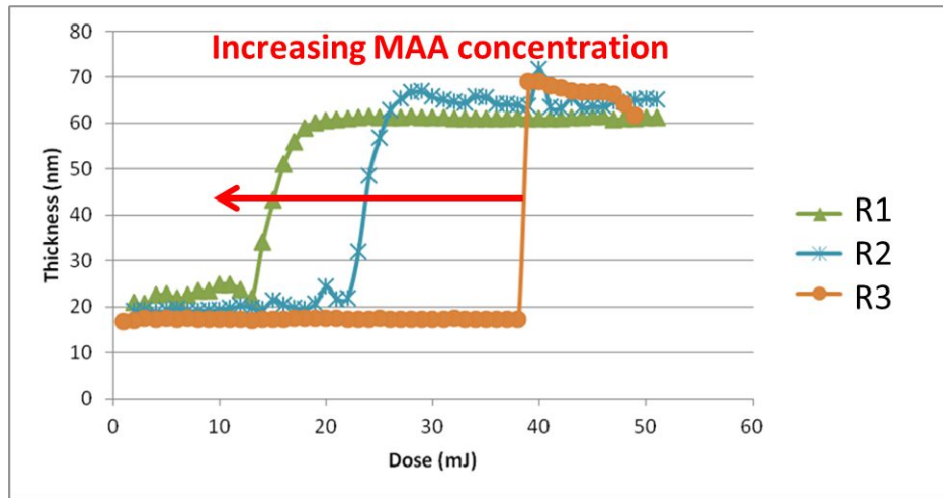


Figure 3. EUV contrast curves of Hf-MAA/BZA with different ratios of MAA:BZA

In order to fully understand the patterning trends observed, it is necessary to probe the mechanism of these materials. During UV exposure, triflic acid is generated from the decomposition of the PAG molecule. In order to investigate the chemical changes occurring during acid generation, these conditions were simulated by adding triflic acid to a solution of HfO_2 nanoparticles and measured with ^1H NMR. The proton NMR spectrum for the HfO_2 -MAA control is shown in

the bottom of figure 4. The peak at 1.9 ppm corresponds to the methyl protons, while the peaks at 5.8 and 6.1 correspond to the two protons on the pendant vinyl group. These broad peaks, slightly shifted upfield, represent methacrylate ligands bound to the nanoparticle core. The top spectrum, HfO₂-MAA particles spiked with triflic acid, shows peaks corresponding to a portion of ligands still attached to the core, but also the formation of a different species of methacrylate. Verified by the proton NMR spectrum of a mixture of methacrylic acid and triflic acid (not shown), these new peaks correspond to unbound methacrylic acid. This indicates that the methacrylate ligands are liberated from the particle surface in the presence of triflic acid.

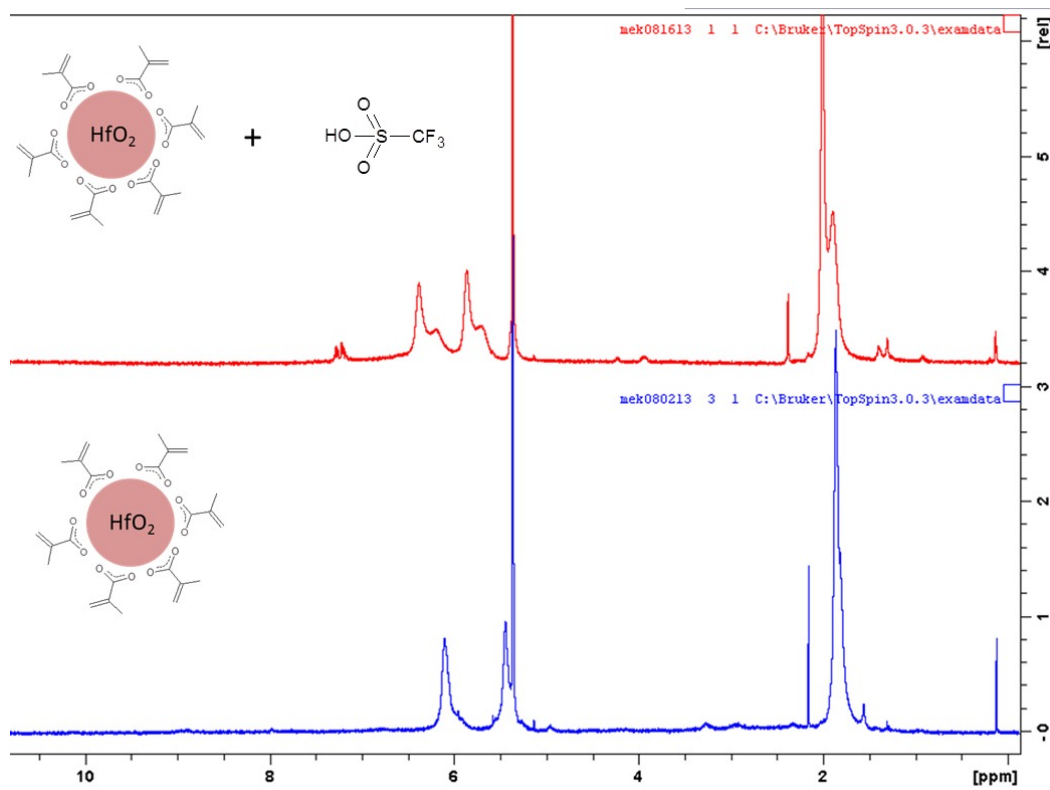


Figure 4. ¹H NMR spectra of HfO₂-MAA and triflic acid-spiked HfO₂-MAA

Fourier Transform- Infrared (FT-IR) spectroscopy was also used to probe chemical changes after UV exposure. While NMR experiments were conducted in solution, FT-IR experiments were carried out using films on silicon wafers, to directly observe chemical changes in the film upon exposure. Figure 5 shows overlaid transmission spectra of unexposed and UV exposed (254 nm) HfO₂-MAA/BZA resist films. The peaks at 1538 and 1439 cm⁻¹ correspond to the stretching modes of the bound carboxylate ligand. After UV exposure, the intensity of the bound carboxylate peaks decreases, indicating a loss of bound ligands after exposure. This data corroborated the proton NMR data, further supporting the theory of ligand displacement upon generation of triflic acid.

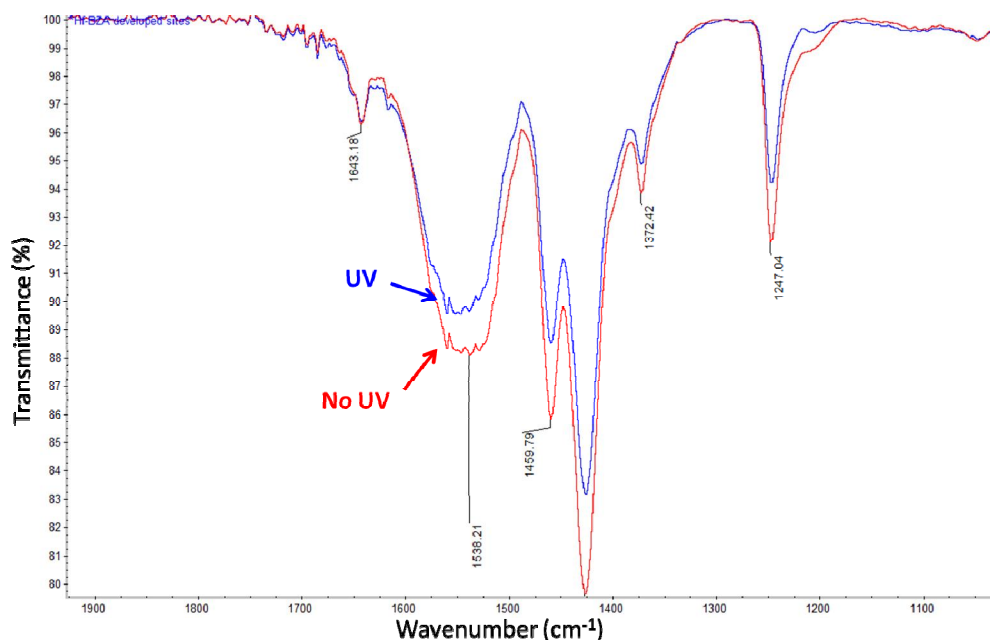


Figure 5. FT-IR Spectra of Hf-BZA films before and after UV exposure

One noteworthy result of the FT-IR experiments was the before/after UV exposure spectra for HfO₂-MAA/BZA resist with PAG showed the same intensity drop in the carboxylate region as the HfO₂-MAA/BZA resist without PAG. Comparing EUV patterning data of formulations with and without PAG yielded remarkable results. Figure 6 shows images of patterned HfO₂-MAA/BZA with and without PAG. These formulations show comparable sensitivity and resolution, indicating that the particles with a ligand mixture do not require a PAG achieve the same level of performance.

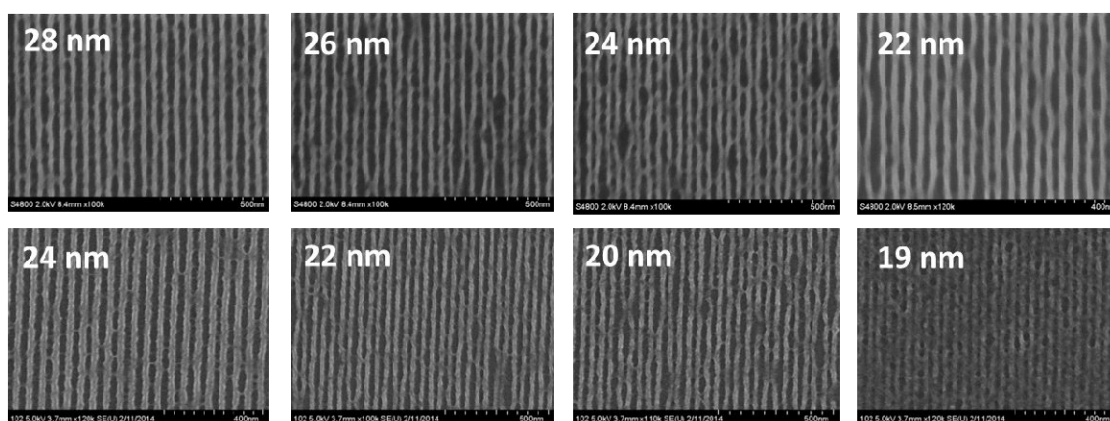


Figure 6. SEM images of EUV patterned HfO₂-MAA/BZA with PAG (top row) and without PAG (bottom row), dose 38 mJ

Previously, Ober et. al. reported a ligand exchange mechanism, in which the generated triflic acid exchanges with a methacrylate ligand⁶. While this is likely occurring during exposure of the resist composition containing PAG, it may be part of a set of chemical reaction occurring simultaneously, based on data presented in the paper.

Both the spectroscopic and patterning data obtained have led to the formulation of a complex patterning mechanism, illustrated in figure 7. The PAG-free mechanism, following the right side of the mechanism flow, involves a ligand ejection by photo decarboxylation. This mechanism has recently been reported for Group IV metal oxo-cluster resists⁷, and is a plausible theory for the dissolution contrast observed in the absence of a PAG.

By focusing on and modifying the key structural components identified by this study, optimization of the nanoparticle resists can further improve their lithographic performance. Modulation at 15 nm half-pitch resolution with a dose of 38 mJ was achieved with the HfO₂-MAA/BZA resist, depicted in figure 8. These results warrant continued investigation into novel resist architectures to enable continued progress in EUV resist development.

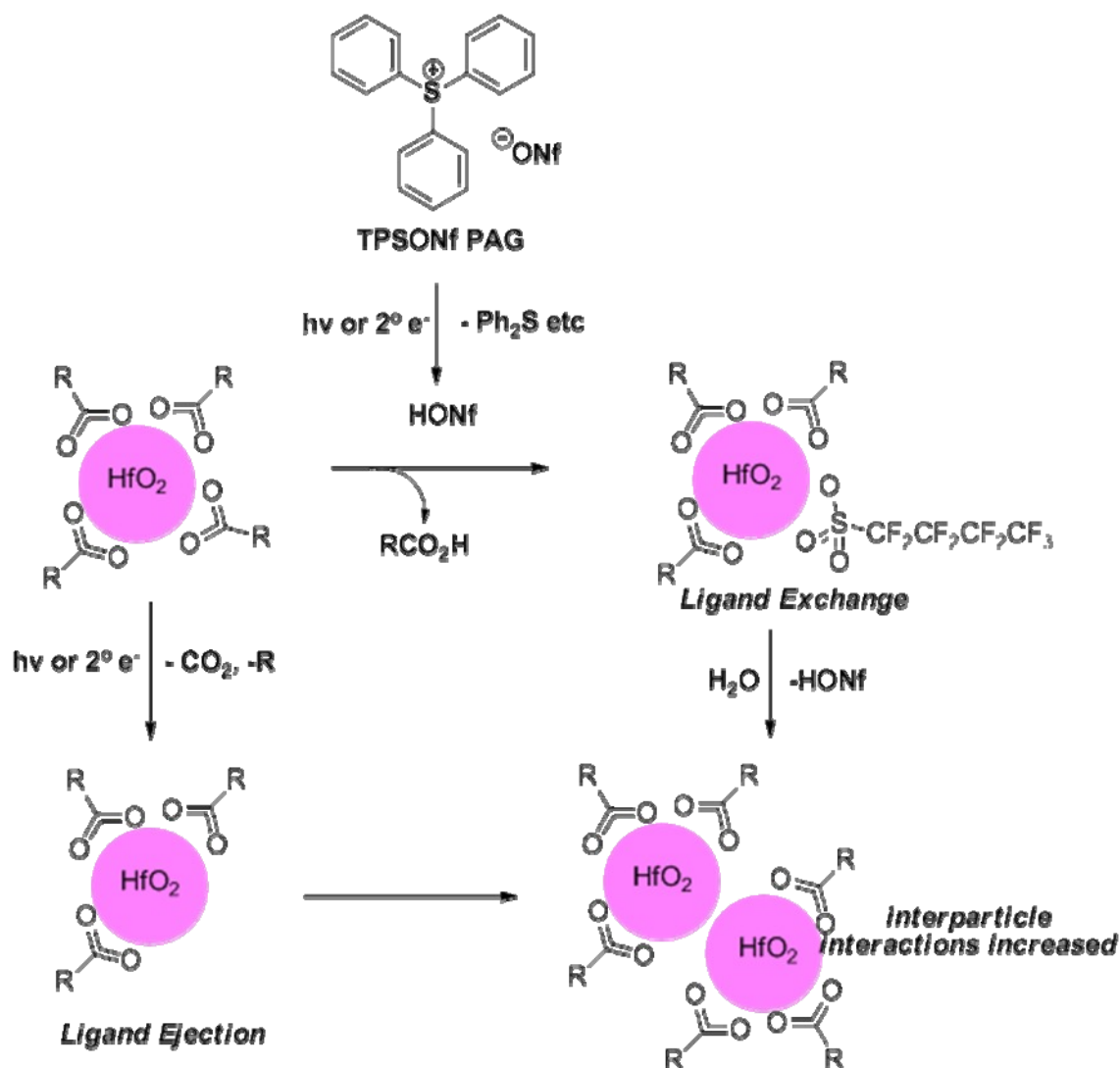


Figure 7. Schematic of proposed patterning mechanisms

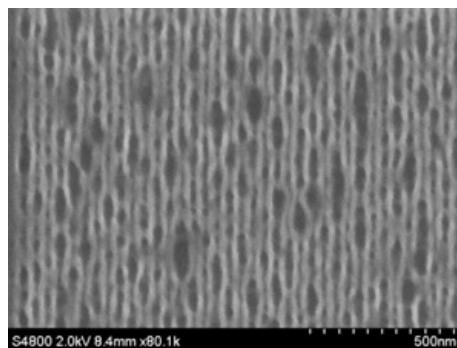


Figure 8. High resolution SEM image of HfO₂-MAA/BZA resist, 15 nm half-pitch, 38 mJ

4. CONCLUSIONS

The effects of structural components of metal oxide nanoparticle resists were studied. Through synthesis of nanoparticles with varied cores and ligands, it was discovered that the EUV patterning performance depends prominently on the type of organic ligands, while the metal in the core has little to no effect on the resolution or sensitivity of the resist. Both the ligand structure and the ratio Spectroscopic and patterning data has led to the formulation of a complex patterning mechanism involving ligand ejection, initiated by secondary electrons from EUV exposure, and ligand dissociation, initiated by photo-generated acid. Though further experimentation and optimization is required, modulation at 15nm half-pitch shows promise that these resist systems have the capability to resolve high resolution features with modest sensitivity.

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