

Chapter 8

Photoresists for EUV Lithography

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Notes and References

8.1 Introduction

Extreme ultraviolet lithography (EUVL) has advanced dramatically since its inception in 1986. Progress in EUV research has required an interdisciplinary approach involving partnerships of scientists and engineers within both industry and academics. Contributions from the fields of physics, optics, computer science, business, materials science, and chemistry have been critical to all phases of EUV technical advances.

One of the most important components of EUVL is the technological advancement of photoresists. Although EUV photoresist performance has made dramatic advances over the years, resist requirements are extremely demanding. Since the first edition of this book came out in 2008,¹ several technical challenges have been met in all areas of technology to advance EUVL for use in high-volume manufacturing (HVM) fabs. Most notable have

Table 8.3 Summary of characteristics for three Schwarzschild cameras and resist results.

Wavelength (nm)	Optic		PMMA Resist			PN114 Resist	
	Reflective Surface	NA	Absorbance* (1/ μm)	E size (mJ/cm ²)	Sidewall Angle	Absorbance* (1/ μm)	Sidewall Angle
37.5	Iridium	0.113	37	80	19 deg	—	—
13.9	Mo/Si Multilayer	0.0835	5.95	66	65 deg	4.4	Undercut ~75 deg
6.8	Ru/B4C Multilayer	0.07	1.2	—	87 deg		Nearly Vertical

*Absorbance values taken from Kubiak et al.,²⁷ except PMMA at 37.5 and 6.8 nm, which were calculated.^{16,17}

Table 8.3 shows the results of printing 500-nm dense lines in 60-nm-thick PMMA. Sidewall angles were measured using scanning tunneling microscopy (STM) and by measurement of cross-section SEMs. PMMA optical density was determined experimentally by Kubiak^{22,27} or through calculation.^{16,17} The PMMA absorption coefficient increases dramatically with increasing wavelength; consequently, the sidewall angle decreases at longer wavelengths. Wood et al. concluded that wavelengths shorter than 13.9 should be pursued for increased transparency and steeper sidewall angles, and they also concluded that bilayer or trilayer resist schemes may be necessary for EUVL to remedy problems such as pinholes and low etch resistance.

8.3 Absorption Coefficients of EUV Photoresists

The absorption of imaging light is one of the most important resist properties.²⁸ Photoresist absorption of EUV light is just as important as in the previous four lithography wavelengths; however, the mechanism by which EUV photons are absorbed is very different from the mechanisms for absorbance of longer wavelengths (157 to 365 nm). At longer wavelengths, the light interacts with the molecules in the resist by exciting an electron from a filled molecular orbital to an empty orbital (Fig. 8.5). In EUVL, however, the 92-eV photons remove electrons from the molecule, creating high-energy electrons (~80 eV) and holes. One important consequence of these mechanistic differences is that the EUV absorption is primarily determined by the elemental composition and mass densities of the resist—not the precise arrangement of these elements within the molecule (its structure) as it is at longer wavelengths.

8.3.1 Definitions of transmission and absorption

The absorption by the film depends both on the resist thickness t and the absorbance A , also referred to as the absorption coefficient, of the resist material. The absorbance A is a per-unit distance, and t must be in the same distance units. For resist films, t is usually in microns and A is per micron.

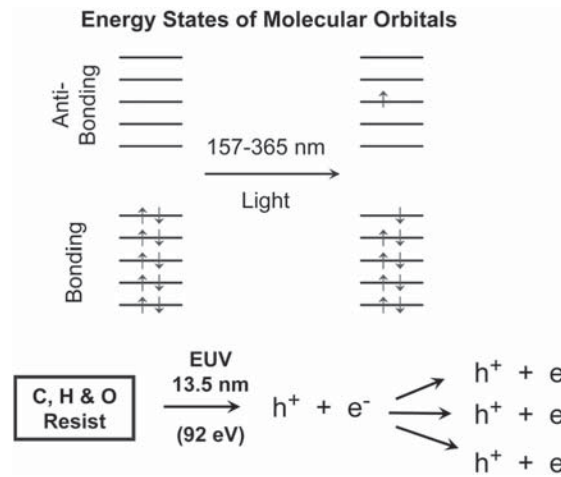


Figure 8.5 Comparison of exposure mechanisms at EUV and longer wavelengths (reprinted from Ref. 1).

A source of great confusion is the fact that absorbance using both the base e and the base 10 definitions are in common practice. Care must be exercised in comparing literature values for absorbance since the base e value will always be 2.303 times larger than the value reported at base 10. Whenever possible, base e values will be used in this chapter. The transmission and absorption of a resist film are defined as

$$\text{Transmission} \equiv I/I_o = e^{At}, \quad (8.2)$$

$$\ln(I_o/I) = At = 2.303 \log(I_o/I), \quad (8.3)$$

$$\text{Absorption} = 1 - \text{Transmission}. \quad (8.4)$$

In Eqs. (8.2)–(8.4), I_o is the incident light intensity, and I is the intensity after the light has passed through the resist film. A is the absorbance per unit thickness, and t is the thickness of the film, so At is a dimensionless number specific to a particular film thickness. The absorbance A is equivalent to the sum of the Dill A and Dill B parameters. For EUV absorption there is no bleaching of the resist film, so the Dill A parameter is 0. Thus, the absorbance A is the same as the Dill B parameter.

8.3.2 Early absorption goals

The atomic absorption cross-section tables published by Henke, Gullikson, and Davis^{16,17} have been the cornerstone for many of the absorption values determined in EUVL. A qualitative representation of absorption coefficients of many of the elements in the periodic table provides insight into the relationship between absorption and chemical composition (Fig. 8.6).²⁹

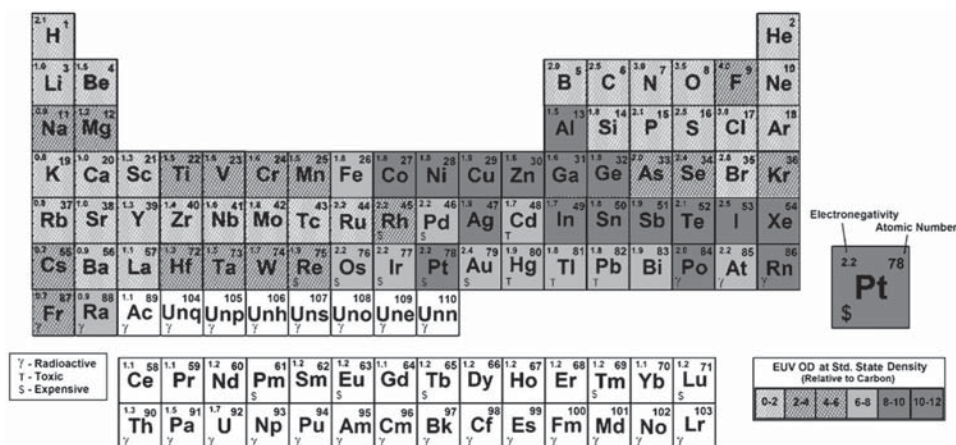


Figure 8.6 The periodic table with respect to EUV optical density (reprinted from Ref. 29).

Heavy elements tend to be darker than light elements. Historically, developing resists for new imaging wavelengths has always involved a struggle to find resist materials that were transparent enough to provide straight sidewalls in printed features. For example, transparency has been an important principle driving the development of new polymers for i-line (365 nm, novolaks), deep ultraviolet (DUV) (248-nm, polyhydroxystyrene), 193-nm (aliphatic esters), and 157-nm (fluoropolymers) lithographies. Similarly, during the first years of EUVL, when resist films were 100–300 nm thick, resist chemists made a number of efforts to increase the transparency of the resists. In 2004, Dai and Ober developed a boron-containing photoresist with the idea that its high transparency at EUV wavelengths was desirable.³⁰ In 2006, Kwark et al.³¹ measured absorbance of resist films and suggested not only that low absorbance was desirable, but that lowering the density of resist films might be a good way to achieve this.

8.3.3 A Change in absorption goals: from light to dark

Three key papers in 2008 caused the resist community to reconsider their efforts to make more-transparent resists and to instead make darker resists. Kozawa et al. did a study of 22-nm line-and-space (L/S) imaging using EUV light, focusing on the tradeoff between sensitivity, resolution, and line edge roughness.³² The researchers found that for resist systems formulated for low doses, there was not enough contrast in the latent image and unacceptable line edge roughness would be expected, assuming imaging was still feasible. They recommended increasing resist absorption and/or acid generation efficiency per photon. Sasaki et al. investigated EUV resists made with main-chain fluorinated polymers with the idea that this would increase EUV absorbance and thus increase EUV photospeed.³³ These authors found that the fluorinated

polymers gave up to 10X better photospeed than nonfluorinated polymers. Additionally, they detected small amounts of HF in the fluorinated polymers after exposure to EUV light, but did not determine the extent to which this contributed to the improvements in photosensitivity.

In 2008, Gronheid, Van Roey, and Van Steenwinckel investigated EUV resist performance as a function of resist thickness.³⁴ They found that linewidth roughness (LWR) increased as films got thinner and attributed this to reduced absorption of EUV light by the thinner films. Gronheid et al. continued this work in 2009³⁵ and suggested that the best optical density for printing 22-nm dense lines in 50-nm resist films is 10/ μm . This recommended absorbance was much larger than the absorbance of the commercial EUV resist (3.88/ μm) they were using at the time.

In 2011, Thackeray discussed absorbance of EUV resists and proposed using fluorine to increase absorbance.³⁶ However, he noted that for the resist thicknesses needed for sub-20-nm imaging, even perfluorotetraethylene would not have as much EUV absorption as is desirable. He noted that non-chemically amplified resists could reduce noise in imaging and thus reduce LWR, but that they typically had slow photospeeds. In this time frame, many other papers also proposed increasing EUV resist absorbance. For example, in 2011 Yamashita used fluorine to do this,^{37,38} in 2012 Ongayi reported using polymer-bound fluorine containing chromophores to increase absorption,³⁹ and in 2013 Christianson also used fluorinated materials with the goal of increasing absorbance.⁴⁰

Despite the high absorptivity of metals (Fig. 8.6), and published demonstrations of EUV-sensitive, metal-based resists, no one proposed metal-based resists as a solution for getting enough EUV absorption until Neisser, Cho, and Petrillo suggested it in 2012.⁴¹ Metal-based EUV resists have proved to be a promising and active area of research and are discussed in Section 8.8.

8.3.4 Measuring absorption of actual resist films

The measurement of resist film absorption can be done by several methods. One way is to do a straightforward absorption measurement. One of the first measurements of this kind was done in 1992 by Kubiak et al.,²⁷ who determined the absorbance of several thicknesses (75 to 500 nm) of PMMA coated on 360-nm thick membranes of Si_3N_4 . Another example is the 2007 work by Garg, Antohe, and Denbeaux.⁴² In 1999, Matsuzawa et al.⁴³⁻⁴⁵ combined Bicerano's graph-theoretical⁴⁶ method for calculating polymer density with the Henke elemental absorption coefficients^{16,17} to predict the absorption coefficients of 150 polymers using EUV light (13.5 nm). The researchers found that polymers used in i-line, DUV, and 193-nm photoresists all had roughly similar transmission of $\sim 30\%$ for 300-nm films, and $\sim 65\%$ for 100-nm films, respectively. As expected, they found that low density made

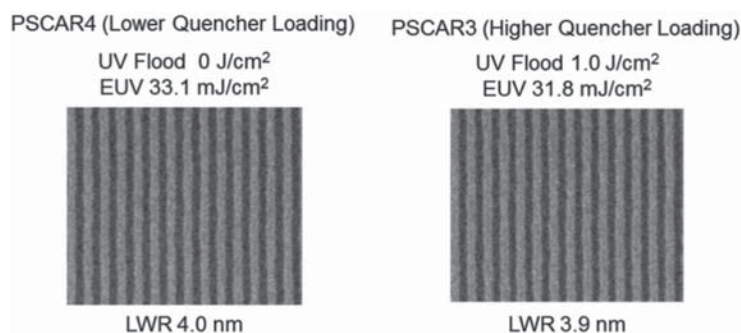


Figure 8.34 Comparison of printing 15 nm L/S patterns between a low-base PSCAR without flood exposure and a high-base PSCAR with flood exposure dose (reprinted from Ref. 142).

8.7.6 Conclusions

Acid amplifiers. Acid amplifiers have been developed in an effort to help make progress against the RLS tradeoff by creating more acids per absorbed photon. Although AAs existed prior to their use in EUVL,¹³¹ this section describes the creation of new AAs specifically designed to work in chemically amplified EUV photoresists. A number of design strategies have been used to create stable AAs that create strong, fluorinated acids that can be added to existing resists, or can be bound to polymers.

PSCAR. The PSCAR platform is much newer than the AA platform; therefore, it is currently an area of active research. Overall, it is an elegant and creative approach to solving the RLS tradeoff using an acid-deprotectable photosensitizer precursor that has clearly demonstrated a capacity for improving photosensitivity.

Summary. A number of lithographic experiments have shown that AAs can improve the overall RLS (Z-parameter) performance of resists versus control resists, and the PSCAR platform has shown dramatic improvements in sensitivity. However, two questions remain: (1) Neither approach improves the photon statistics of absorption; therefore, are they capable of beating the RLS tradeoff? (2) Are AAs and PPs only capable of making bad resists better, or are they also capable of making good resists great?

8.8 Metal-Containing Resists

Since 2009, the photoresist community has shown a great deal of interest in EUV photoresists containing metallic elements. This recent interest in metal-containing resists was most likely initiated by three circumstances:

1. Key, high-profile papers by Doug Keszler at Oregon State University (OSU)^{147,148,227} and Chris Ober at Cornell University^{149–158}

demonstrated that hafnium oxide (films or nanoparticles, respectively) could act as good EUV photoresists.

2. The realization that capturing more EUV photons (higher OD as discussed in Section 8.31) will be essential to provide manufacturing capabilities with the necessary photon statistics.^{36,159} Additionally, since second-row elements (e.g., C, O, N, F) are relatively transparent to EUV light, other elements must be used.
3. The maturation of EUVL has convinced resist companies around the world to assign more chemists to invent better EUV resists, prompting the investigation into more exotic resist designs.

This section will describe multinuclear (two or more metal atoms/molecule) materials followed by mononuclear (one metal atom/molecule) resist systems. Due to space limitations, resists containing less than 1 atomic % metal and/or resists for which the photochemistry does not involve the metal center will not be included.^{160–162}

8.8.1 Metal oxide resists from Oregon-State University and Inpria

The e-beam imaging capability of metal-oxide resists developed by Keszler and coworkers at OSU was first published in 2009.²²⁷ These researchers described metal-oxide films (not nanoparticles) composed of peroxo-modified forms of hafnium oxide sulfate (HafSOx) or zirconium oxide sulfate (ZircSOx) that showed e-beam sensitivity ($D_{0.8}$ =dose to 80% thickness using 30 keV e-beams) as low as 21 and 7.6 $\mu\text{C}/\text{cm}^2$, respectively. These relatively fast resists had molar metal-to-sulfate ratios of $\sim 2:1$. The ZircSOx resist printed 16-nm isolated lines and 28-nm dense lines with LWRs of 3.4 and 6.4 nm, and with doses of 112 and 50 $\mu\text{C}/\text{cm}^2$, respectively, using the same 2:1 of metal to sulfate ratio [Figs. 8.35(a) and (b)]. When the metal-to-sulfate ratio is reduced to 1.4:1, the LWR improves but at a cost to sensitivity. These resists printed 15-nm isolated lines and 32-nm dense lines with LWRs of 1.9 and 2.1 nm, and with doses of 999 and 810 $\mu\text{C}/\text{cm}^2$, respectively. Additionally, the HafSOx and ZircSOx resists were evaluated for etch resistance versus that of thermally grown SiO_2 . The authors found that these metal oxide resists etch $9\times$ and $7\times$ slower than the SiO_2 control, respectively. Commercial work on these metal-oxide resists has been done by the Inpria Corporation.

The key to the photoreactivity of the HafSOx resists appears to be controlling the dehydration reaction [Fig. 8.36(a)], which crosslinks and thereby reduces the solubility of these metal oxo-films.¹⁴⁷ This dehydration reaction is inhibited by binding peroxide to Hf. Fortunately, the metal peroxide decomposition can be induced by high-energy light or electrons [Fig. 8.36(b)], thereby creating metal hydroxides that can condense and become insoluble. In brief, the metal peroxides allow the resists to dissolve in the unexposed regions,

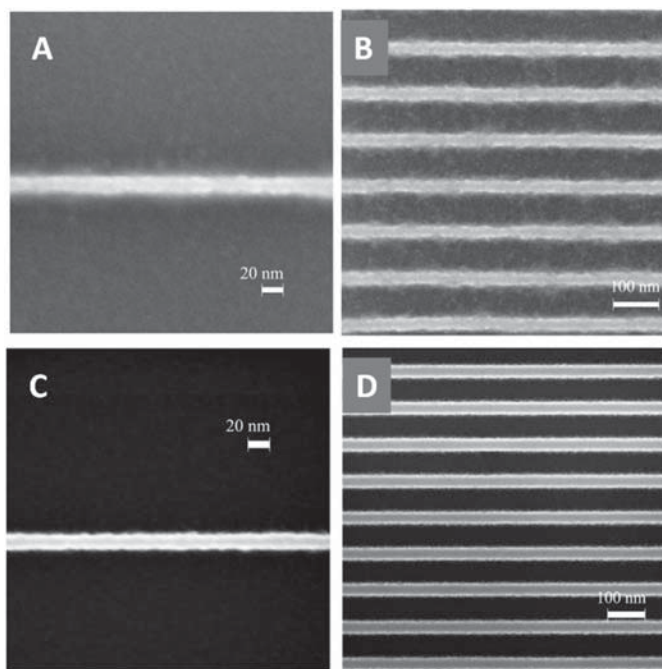


Figure 8.35 SEM images of ZircSOx resist films exposed with 30-keV electron beams: (a) metal/sulfate = 2.0, 16-nm isolated line, dose = 112 $\mu\text{C}/\text{cm}^2$; (b): metal/sulfate = 2.0, 28/72-nm lines and spaces, dose = 50 $\mu\text{C}/\text{cm}^2$; (c) metal/sulfate = 1.4, 15-nm isolated line, dose = 999 $\mu\text{C}/\text{cm}^2$; (d) metal/sulfate = 1.4, 36/64-nm lines and spaces, dose = 810 $\mu\text{C}/\text{cm}^2$ (reprinted from Ref. 227 with permission; © 2009 Elsevier).

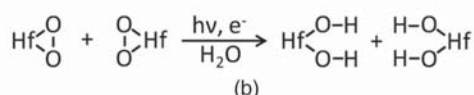
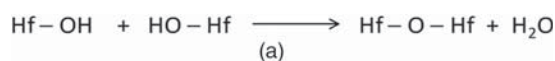


Figure 8.36 Proposed mechanisms for OSU/Inpria resists: (a) dehydration mechanism and (b) photomechanism (reprinted from Ref. 147).

and upon photolysis the metal peroxides become metal hydroxides and condense to become insoluble features of the negative-tone resists.

The first manuscript to describe EUV imaging of these OSU/Inpria metal-oxo resists on the Berkeley MET showed 22-nm posts and 22-nm lines with modulation down to 15 nm (Fig. 8.37).¹⁴⁸ Later, Ekinci and coworkers from the Paul Scherrer Institut (PSI) demonstrated the remarkable imaging capabilities of Inpria XE151JB and XE151IB using EUV interference lithography. These resists printed dense lines from 22–16 nm with doses of 75–80 and 160–200 mJ/cm^2 , respectively (Fig. 8.38). The LER of XE151JB

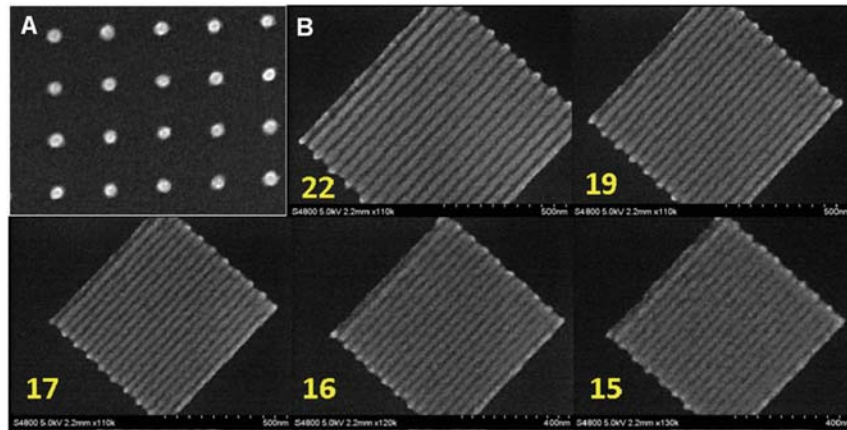


Figure 8.37 SEM images of patterns printed using the Inpria metal-oxide resist: (a) 22-nm posts printed using conventional annular illumination; (b) 22- to 15-nm dense lines printed using pseudo-phase shift mode on the 0.3-NA Berkeley MET (reprinted from Ref. 148).

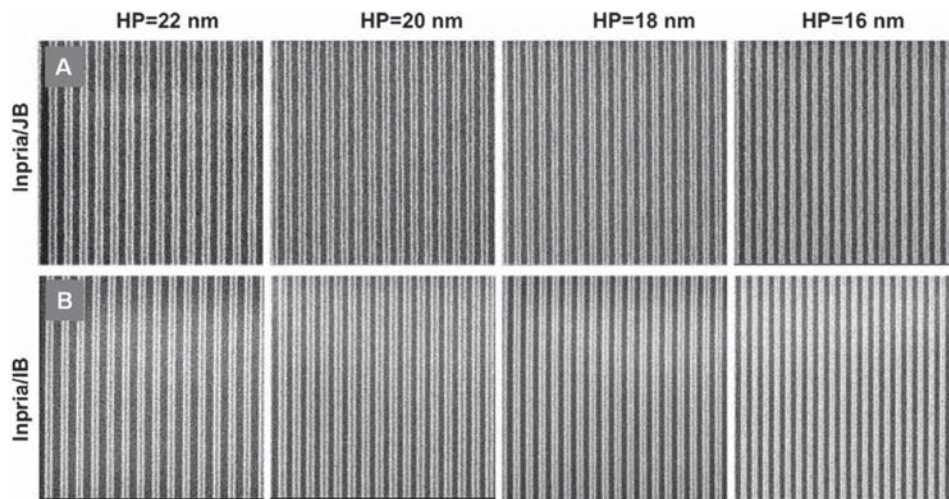


Figure 8.38 SEM images printed using Inpria/OSU resists as imaged by interference lithography at the PSI: (a) Inpria/JB resist and (b) Inpria/IB resist (reprinted from Ref. 163).

was determined to be 2 ± 0.5 nm. Furthermore, XE151JB and XE151IB could resolve 12- and 8-nm dense lines at doses estimated to be ≥ 80 and ≥ 200 mJ/cm², respectively (Fig. 8.39).

Hafnium oxide and zirconium oxide nanoparticle resists. Research by C. Ober, E. Giannelis, and coworkers at Cornell University demonstrated several unique resist systems based on HfO₂ or ZrO₂ nanoparticles with carboxylate ligands (Fig. 8.40).^{149–158} These interesting and unique resists exhibit negative-tone imaging upon exposure to DUV, 193-nm, EUV, and

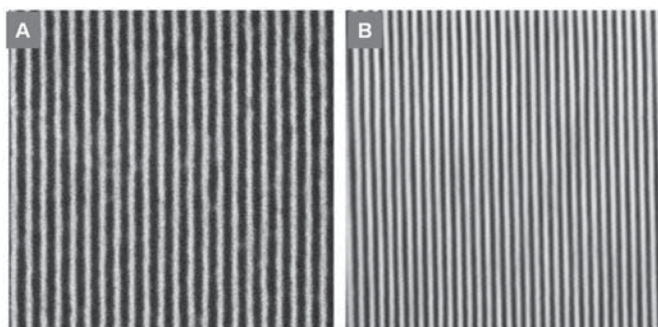


Figure 8.39 SEM images of (a) 12-nm half-pitch dense lines printed using the Inpria/JB resist and (b) 80-nm half-pitch dense lines printed using the Inpria/IB resist (reprinted from Ref. 163).

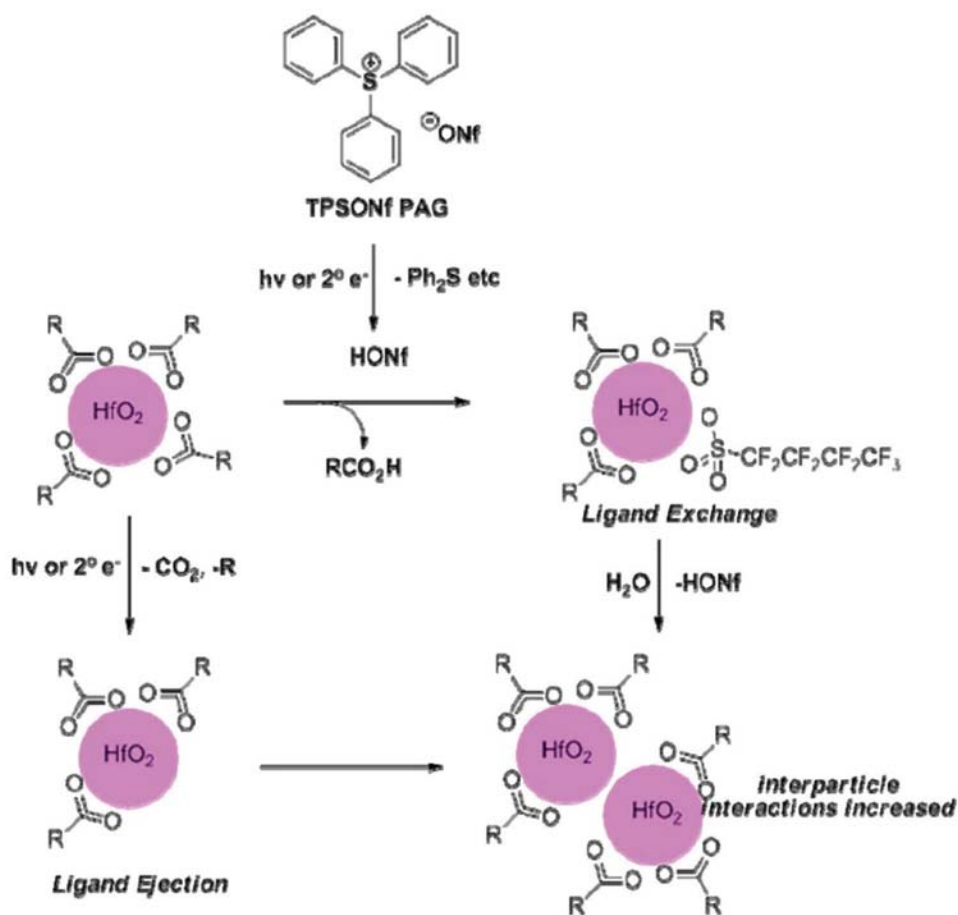


Figure 8.40 Photomechanism of negative-tone HfO_2 nanoparticle resists (reprinted from Ref. 155).

e-beam radiation. Furthermore, these resists can also produce positive-tone imaging using wavelengths of 193-nm and DUV when processed using post-exposure bakes.

The earliest versions of these resists were prepared using methacrylate $[-O_2CC(CH_3)=CH_2]$ as a ligand and formulated with either PAGs or free-radical initiators. Although the use of methacrylate ligands suggest that the negative-tone imaging mechanisms might involve free-radical crosslinking, careful spectroscopic, thermodynamic, and mechanistic studies reveal that the negative-tone solubility switches do not involve free-radical crosslinking, but instead involve a ligand exchange mechanism that can proceed without PAGs [Fig. 8.40 (left)] or with the assistance of PAGs [Fig. 8.40 (right)].^{153,155–158,164}

These nanoparticle resists have good EUV patterning capability at extremely fast photospeeds. Recently, Ober and coworkers demonstrated the imaging capabilities of HfO_2 and ZrO_2 nanoparticle resists prepared with trans-dimethylacrylic acid as a solubilizing ligand and containing 3 wt % non-ionic PAG (Fig. 8.41).¹⁵⁶ 20- and 30-nm isolated lines were printed using doses of 2.4 and 1.6 mJ/cm^2 , for HfO_2 and ZrO_2 , respectively. Although the LER values of these resists are modest (5–7 nm), the LER is not too poor, considering that the resists are extremely sensitive and are composed of nanoparticles that are 1–2 nm in diameter.¹⁴⁹

8.8.2 Tin oxide cluster resists from CNSE

Cardineau, Brainard, and coworkers described the synthesis and lithographic evaluation of thin films of tin-oxo clusters $[(RSn)_{12}O_{14}(OH)_6]X_2$ [Fig. 8.42(a)], using EUV light (13.5 nm).^{165,166} These tin clusters consist of spherical tin-oxo cages in which each tin atom is covalently bound to one

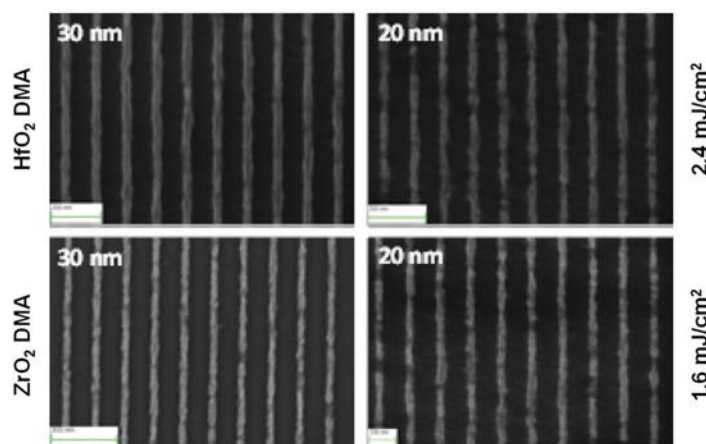


Figure 8.41 Imaging capability of HfO_2 and ZrO_2 nanoparticle resists (reprinted from Ref. 156 with permission from The Society of Photopolymer Science and Technology).

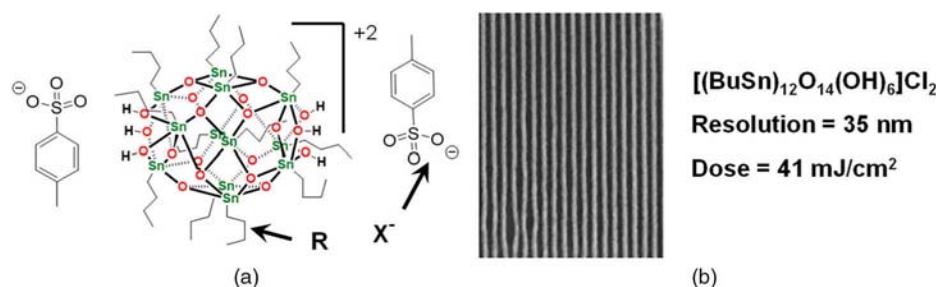


Figure 8.42 The mechanism of photolysis for tin clusters of the type $[(\text{RSn})_{12}\text{O}_{14}(\text{OH})_6]\text{X}_2$ was explored through structural variation. (a) Clusters were made varying the bond energies of both the counter-ions (X) and the organic ligands (R), and tested for EUV lithographic performance. (b) 35-nm dense lines printed using $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2$ (reprinted from Ref. 166).

organic (R) group. The clusters have a +2 charge and are typically precipitated with pairs of anions (X). Furthermore, these new resists should be relatively dark since both tin and oxygen readily absorb EUV photons with optical densities that are $10.5\times$ and $1.7\times$ greater than carbon (Fig. 8.6).^{16,17}

Lithographic results. In an initial study, the tin-oxo cluster $[(\text{n-BuSn})_{12}\text{O}_{14}(\text{OH})_6](\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ was dissolved in 2-butanone and spin-coated into a thin film. The film was exposed to EUV light in an open-field pattern using the Berkeley direct contrast tool¹⁶⁷ (DCT) and developed in 66% aqueous isopropanol solvent for 30 s. This film exhibits negative-tone sensitivity of 20 mJ/cm^2 . The authors also printed 35-nm dense lines by exposing a film of $[(\text{n-BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2$ using the interference lithographic tool at PSI, albeit with a dose of 41 mJ/cm^2 [Fig. 8.42(b)].

Correlation between sensitivity and C-Sn bond strength. The authors evaluated sensitivities of resists prepared with three organic groups bonded to tin: benzyl, butyl and phenyl. One possible reaction that could occur during exposure is homolytic cleavage of the tin-carbon bond. Tin-carbon bonds are relatively weak ($\sim 50 \text{ kcal/mol}$), and tin forms extremely stable radicals; therefore, the authors reasoned that EUV exposure could cause homolysis of the Sn-C bond.¹⁶⁸ Figure 8.43(a) shows the C-H bond dissociation energies of the three hydrocarbons. These C-H bond energies predict the relative stabilization of their radical fragments.

Clusters 8 through 10 were coated on wafers and tested lithographically [Fig. 8.43(a)]. Figure 8.43(b) shows the C-H bond energy versus dose to E_{size} curve for the tin-oxo cluster.¹⁶⁹ In general, the clusters with the weaker C-H bonds show the best sensitivity. By analogy, the authors conclude that the reactivity of the clusters is correlated to the strength of the tin-carbon bonds. This correlation supports a photolysis mechanism in which the homolysis of the tin-carbon bond is involved in the observed change in film dissolution rate.

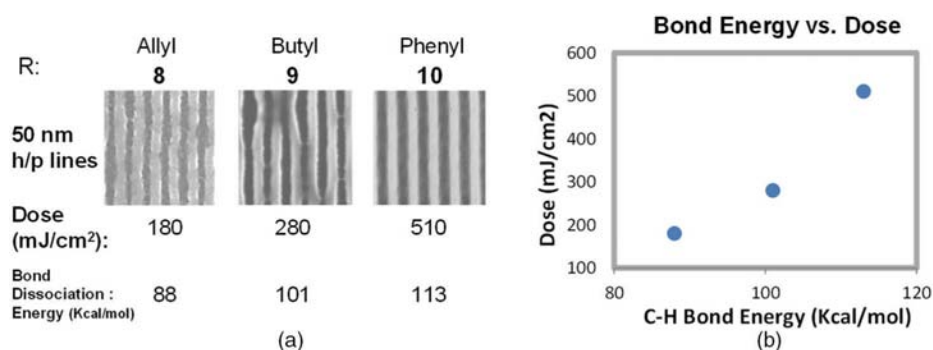


Figure 8.43 (a) The bond dissociation energies for three organic groups and lithographic results. By incorporating these groups into the tin clusters, a broad distribution of Sn-C bond energies should be achieved. (b) For the three clusters tested, there appears to be a direct correlation between the radical stability of the organic group and the sensitivity of the cluster, suggesting that homolysis is occurring (reprinted from Ref. 166).

8.8.2.1 Organo-bismuth oligomers

Passarelli and coworkers developed resists based on bismuth oligomers.^{170,171} Figure 8.44 shows the lithographic capabilities of four of these oligomers. The best resolution was obtained from the dichloride variant (21 nm) and the best

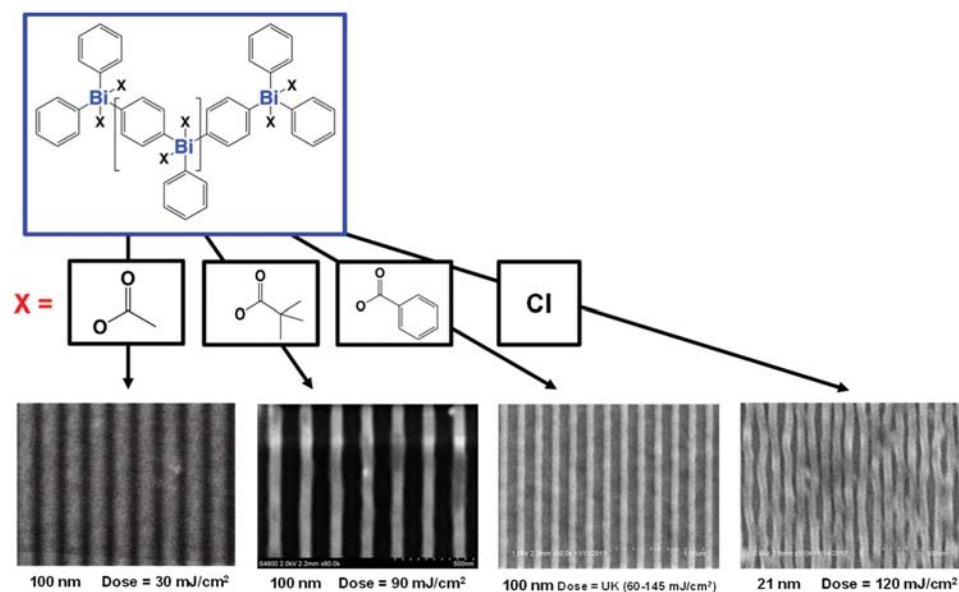


Figure 8.44 Lithographic results for oxidized bismuth oligomer with various X group substituents. Exposures were performed using the LBNL 0.3-NA MET. Dose of 30 mJ/cm² is achieved for X = O₂CCH₃, and a resolution of 21 nm is achieved for X = Cl. The dose for the resist in which X = benzoate was between 60 and 145 mJ/cm² (reprinted from Ref. 170).

sensitivity from the diacetate variant (30 mJ/cm^2). All of the SEM images displayed are of negative-tone development. The authors propose that the negative-tone imaging may result from homolytic cleavage of the Bi-X bond (Fig. 8.44) followed by covalent bond formation between the metal center and aromatic ligand.

8.8.3 Mononuclear-metal resists

Researchers at CNSE and SUNY New Paltz have conducted a broad exploration of resists containing metals with high EUV cross-sections (excluding Hf and Zr studied by OSU, Inpria, and Cornell). The name of this program is Molecular Organometallic Resists for EUV (MORE). Two *multinuclear* resists developed by this program are described in Sections 8.8.2 and 8.8.2.1. This section reviews four resist approaches based on *mononuclear* organometallic complexes. Although these resists have lower concentrations of metal atoms, important photochemical transformations occur at the metal centers and, therefore, provide insight into the kinds of reactions that can occur in metal-containing EUV resists.

Transition-metal oxalates. Freedman and coworkers developed a series of transition-metal oxalates that produce negative-tone resists. One study showed the importance of oxalate loading [versus bipyridine (bpy)] in cobalt complexes.¹⁷² The negative-tone sensitivity of these resists increases dramatically with the number of oxalate ligands (Fig. 8.45). As the number of oxalate ligands increases, so does the negative charge on the transition-metal complex. Authors were not sure which effect was more important for giving good sensitivity: numbers of oxalate ligands or the negative charge.

Another study showed that E_{size} improves as the identity of the central transition-metal changes from chromium to iron to cobalt (Fig. 8.46). Although the ligands are all the same and the oxidation states of the central metal are all the same (+3), as both the number of d-electrons (4, 5, 6) and the optical density of the transition metal (16, 21, 27) increase, the sensitivity improves.

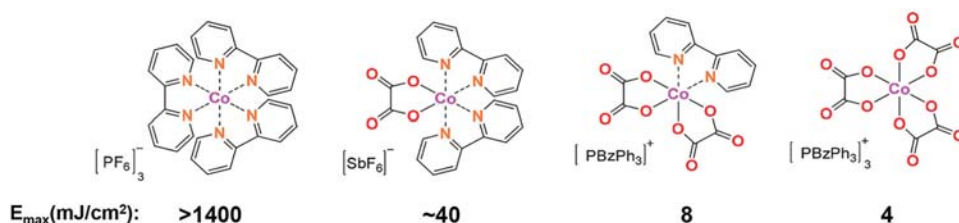


Figure 8.45 Cobalt complexes using bipyridine and oxalate ligands were exposed using an open-frame technique at PSI. The resists improve in EUV photosensitivity when the number of oxalate ligands increases and when the charge on the cobalt complex becomes more negative (reprinted from Ref. 172).

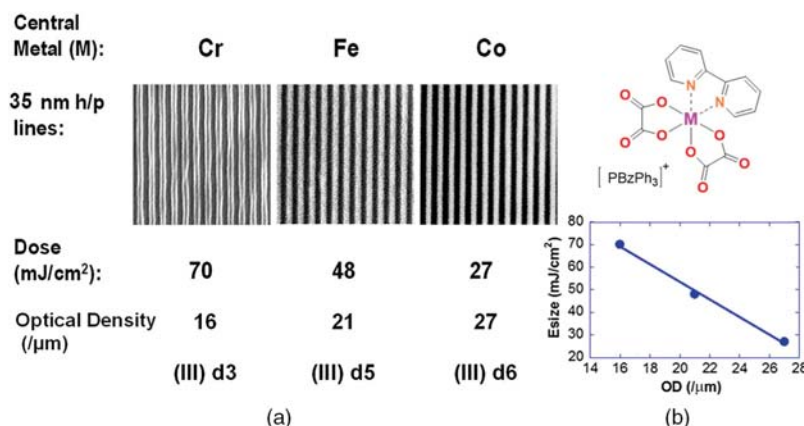


Figure 8.46 (a) EUV imaging capability of resists prepared from three complexes of the type $PBzPh_3 \text{ bpy(ox)}_2M$, where $M = \text{Cr, Fe, and Co}$, versus optical density and number of d-electrons of the central metal. (c) A plot of E_{size} versus optical density of the central metal (reprinted from Ref. 172).

Positive-tone palladium oxalates. Sortland and coworkers developed the first mononuclear positive-tone organometallic resists for EUVL [Fig. 8.47(a)].^{173,174} Positive-tone photoresists are attractive as they allow for dark-field masks in contact hole manufacturing. Dark-field masks are preferred as they minimize flare and are easier to correct for mask defects than bright-field masks. Researchers found that bis-phosphine palladium or platinum oxalates give resists that produce positive-tone images when developed in nonpolar solvents [Fig. 8.47(b)].

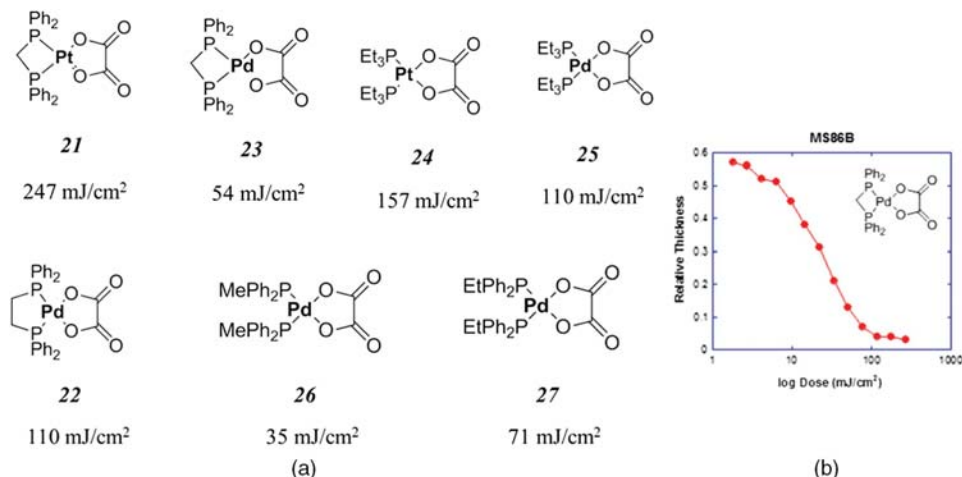


Figure 8.47 (a) E_0 for different platinum and palladium-phosphine oxalates when exposed using the open-frame technique at PSI. (b) Contrast curve of one palladium oxalate resist (reprinted from Ref. 173).

Comparison with solution-phase photochemistry in the literature^{175–177} and exposure of crystals to i-line light by the authors led the authors to propose the exposure mechanism shown in Fig. 8.48, in which metal oxalates create CO₂ as well as zero-valent palladium-phosphine complexes and palladium metal. This photoreaction is consistent with all experimental data, and similar results are found in the literature.^{175,178} The L₄Pd complex is more soluble than the starting material, explaining the positive-tone behavior of this resist system. Unfortunately, palladium metal is insoluble, and the authors were unable to get complete clearing in the exposed regions.

Low-LER dibenzyl tin complexes. Del Re and coworkers developed a series of organometallic tin dicarboxylates [R₂Sn(O₂CR')₂] that print dense L/S patterns with very low LER.^{169,179} Although the sensitivity of many of these compounds is poor ($E_{size} = 50\text{--}600\text{ mJ/cm}^2$), they were capable of good resolution and excellent LER when exposed using interference lithography at PSI. In particular, dibenzyltin dibenzoate [Fig. 8.49(a)] prints 50- and 35-nm dense lines with LWR of 1.7 nm, and dibenzyltin dipivalate resolves 16-nm half-pitch dense lines with 2.1-nm LER and resolves 22-nm half-pitch dense lines with 1.4-nm LER [Fig. 8.49(b)].

Interestingly, these resists seem to show better sensitivity with lower molecular weights, perhaps indicating that higher metal content is important for achieving better sensitivity. We also see a linear trend when we compare molecular weights with E_{max} within a particular compound family (Fig. 8.50).

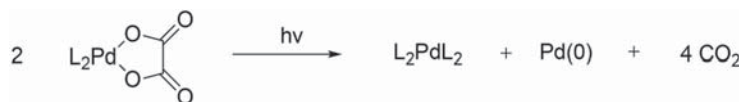


Figure 8.48 Proposed photoreaction for (dppm)Pd(C₂O₄) and (Ph₂EtP)₂PdC₂O₄. The photoreaction is consistent with all experimental data (reprinted from Ref. 173).

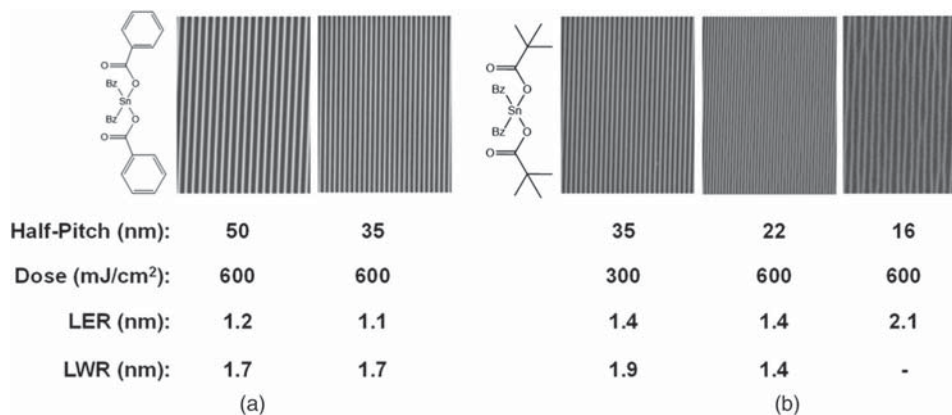


Figure 8.49 EUV imaging capabilities of (a) dibenzyltin dibenzoate and (b) dibenzyltin dipivalate (reprinted from Ref. 179).

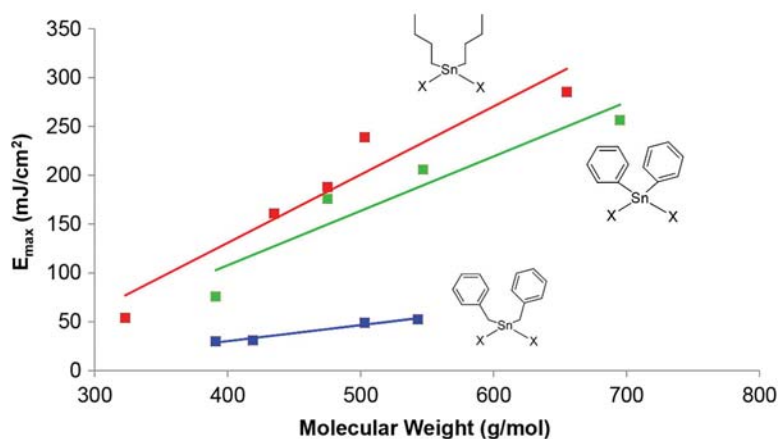


Figure 8.50 Strong correlations exist between sensitivity and molecular weight for $R_2\text{Sn}(\text{O}_2\text{CR}')_2$ complexes when the hydrocarbon moiety (i.e., butyl, phenyl, or benzyl) bonded to tin is the same (reprinted from Ref. 179).

8.8.3.1 High-speed resists using antimony, tin, tellurium, and bismuth

Passarelli and coworkers have presented a series of high-speed, negative-tone resists of the general form $R_n\text{M}(\text{O}_2\text{CR}')_2$ where M is the main-group metal antimony, tin, tellurium or bismuth, and the carboxylate group is capable of undergoing free-radical polymerization (acrylate, methacrylate, or styrene carboxylate). The authors explored the systematic variations of the metal (M), the aliphatic or aromatic R group, and the polymerizable carboxylate group ($\text{O}_2\text{CR}'$) by preparing and lithographically evaluating more than 35 compounds.^{180,181}

One resist, tri(phenyl)antimony diacrylate (JP-20), prints 35-nm lines with modulation down to 16 nm, with sensitivities of 5.6 and 9.2 mJ/cm² when developed in hexanes or water, respectively (Fig. 8.51). This resist exhibits negative-tone imaging in both developers. It has also passed witness plate-based outgassing tests and has excellent shelf-life.

Four resists of the type $\text{Ph}_n\text{M}(\text{acrylate})_2$ and containing antimony, tin, tellurium, or bismuth were synthesized, coated, and evaluated for contrast-curve performance (Fig. 8.52). The relative sensitivities are: antimony produces the fastest resist, then bismuth = tin, and tellurium is the slowest. This sensitivity trend cannot be explained by optical density differences since tin and tellurium are about the same and darkest, then antimony, followed by bismuth. The sensitivity of these resists is, therefore, not merely due to their ability to absorb photons, but also due to other factors explored by the authors.

The authors proposed that these main-group olefin complexes undergo photolysis and solubility changes through a mechanism that involves free-radical polymerization of double bonds (Fig. 8.53). They propose that the initiation involves homolytic cleavage of the M-carboxylate bond followed by

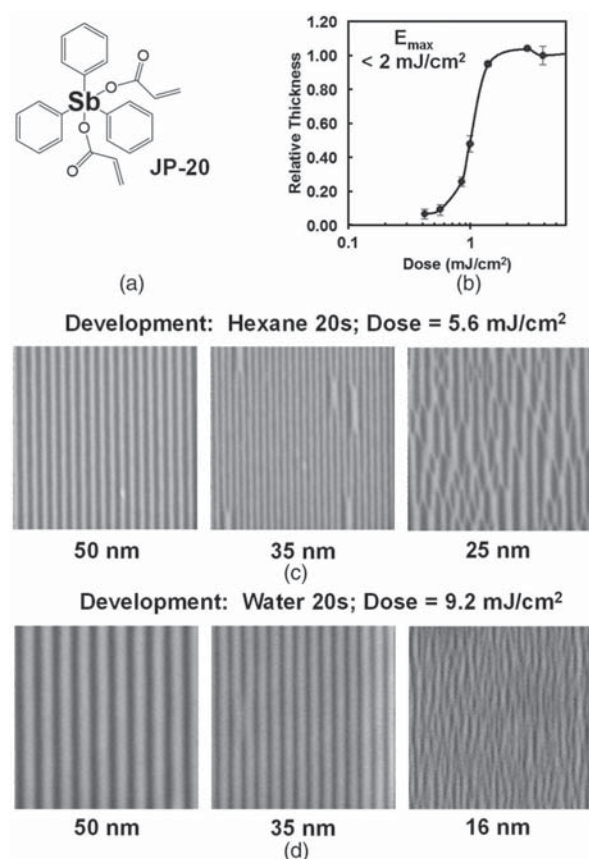


Figure 8.51 Lithographic performance of (a) $\text{Ph}_3\text{Sb}(\text{O}_2\text{CCH}=\text{CH}_2)_2$ (JP-20). (b) High-contrast and high-sensitivity are achieved. (c) JP-20 can be developed in either hexane or (d) water. Both developers produce negative-tone imaging (reprinted from Ref. 180).

polymerization to create linear or branched oligomers within the exposed region. This mechanism is supported by three additional studies: (1) $\text{Ph}_3\text{Sb}(\text{O}_2\text{CH}=\text{CH}_2)_2$ is $\sim 15\times$ faster than $\text{Ph}_3\text{Sb}(\text{O}_2\text{CH}_3)_2$. (2) $\text{Ph}_3\text{Sb}(\text{O}_2\text{CH}=\text{CH}_2)_2$ and $(\text{Cyclohexyl})_3\text{Sb}(\text{O}_2\text{CH}=\text{CH}_2)_2$ have exactly the same photospeed, suggesting that M-C bond cleavage is not involved in the mechanism. (3) The sensitivity of the resist directly correlates to the concentration of olefins in the resist (discussed below).

The authors tested the hypothesis that the greatest contributor to the sensitivity of molecules of the type $\text{R}_n\text{Sb}(\text{O}_2\text{CR}')_2$ is the concentration of polymerizable olefins in the resist. They reasoned that in order for the propagation of free-radical polymerization to proceed, the olefins must be in contact with other olefins, and that higher concentrations of olefins would lead to higher turnover numbers. Larger turnover number should lead to greater sensitivity because more molecules are reacted per initiation event, and

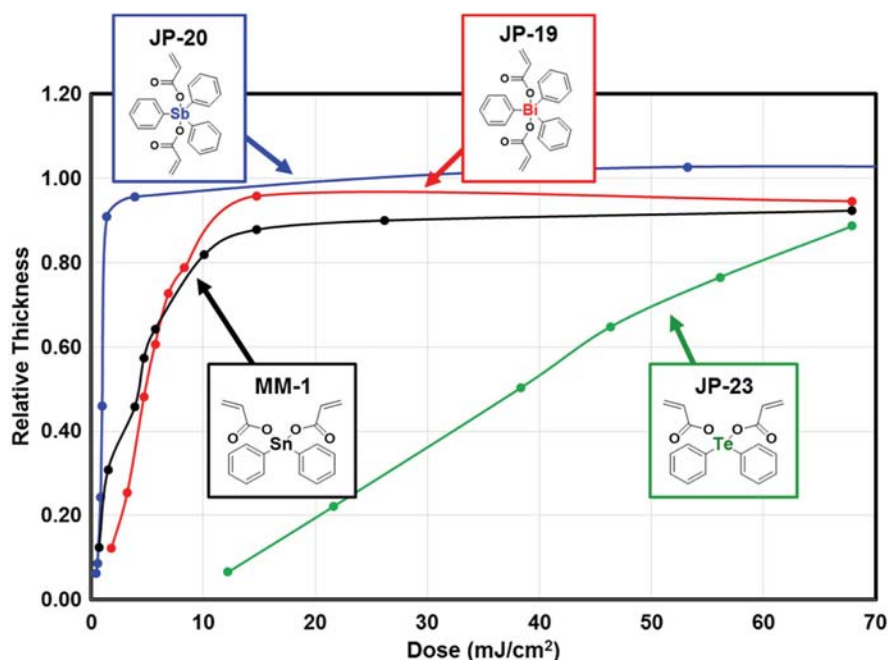


Figure 8.52 Comparison of $\text{Ph}_n\text{M}(\text{Acrylate})_2$ where M = antimony, bismuth, tin, or tellurium. Antimony is the most sensitive (reprinted from Ref. 180).

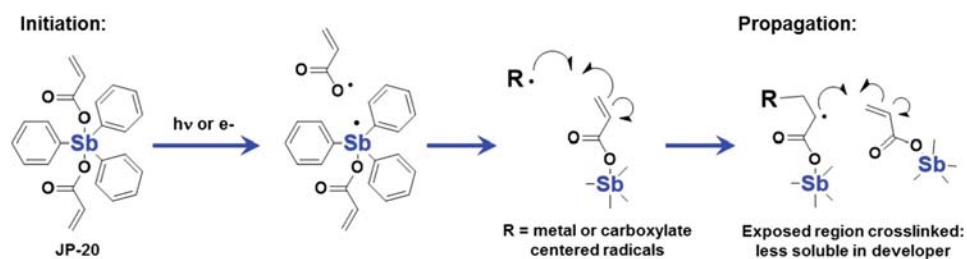
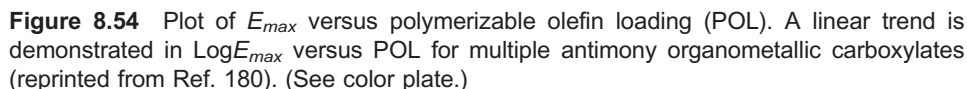


Figure 8.53 Proposed mechanism of an antimony organometallic carboxylate resist system. The authors propose that good sensitivity is achieved through one photochemical homolysis event leading to a cascade of subsequent solubility-changing polymerization reactions (reprinted from Ref. 180).

because higher-molecular-weight molecules have lower solubility. To test this hypothesis, the authors defined a parameter called polymerization olefin loading (POL) as the number of olefins/number of all atoms (excluding hydrogen). A semi-log plot of E_{max} versus POL is shown for 15 resist materials in Fig. 8.54. There is a linear relationship between $\text{Log}E_{\text{max}}$ versus POL, whereas as POL increases, E_{max} decreases (the resist becomes more sensitive). The authors conclude that this correlation is further evidence in support of the imaging mechanism shown in Fig. 8.53.¹⁸⁰



8.9.1 Background: continuous and stochastic models

Figure 8.55 schematically shows the difference between continuum and stochastic models. In Fig. 8.55(a), the absorbed dose distribution is plotted as a continuous function in terms of the number of absorbed photons per unit area in the resist. Figure 8.55(b) is generated by using the value in Fig. 8.55(a) in each 1-nm-square pixel as the average value in a Poisson distribution and then generating a statistical value for the number of absorbed photons in that pixel based on that Poisson distribution. In both graphs, the grayscale indicates the numerical value in each pixel. This physics is the same for any wavelength and any feature size or shape. In reality, the effect of dose on the

The results of calibrated models can match experimental behavior quite well. One set of researchers found that simulated CDs matched experimental values within one nanometer for lines and spaces and within two nanometers for contact holes. Linewidth roughness was predicted with an error of less than one nanometer. The stochastic models show the experimentally observed photospeed to LWR/LER tradeoff quite well and suggest that a lower bound to the LWR and LER is achievable with CARs.

8.11.6 Benchmarking of resists

Many groups have done benchmarking of commercial and experimental EUV resists. Interference imaging gives a much better aerial image than scanner lenses do and is useful for exploring the ultimate resolution of resists. Scanner benchmarking is better for selecting a resist for actual use. While much progress has been made in resists, the benchmarking has consistently shown more LWR and CDU than is desired and a clear tradeoff of photospeed and LWR. The results do show that improved tools and resists optimized for them have improved EUV resist imaging. Given that EUV tools are continuing to improve in many aspects, we can expect better EUV imaging in the future. However, it is clear from all of the benchmarking and science discussed in this chapter that improving EUV noise is much more of an issue than improving EUV resolution. Recent work reported just as this chapter was written suggests that this issue will be worse than might be expected from simple extrapolations of CD variation using the normal distribution,^{225,226} and future EUV imaging is expected to be done with smaller feature sizes, which will also make imaging noise more of a concern. The future of EUVL will be determined by the ability of equipment providers, materials providers, and EUV users to minimize, manage, and accommodate all of the stochastic effects in EUV imaging.

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Robert worked for Polaroid (1987–1990) and at Shipley/Rohm & Haas (1990–2005), where he did product development research in the areas of electrodeposited, dielectric, color filter, DUV, EUV, x-ray, and e-beam photoresists. Robert was the first chemist in the world to design resists for EUVL, starting in 1998 while working at Shipley Co. and in collaboration with the EUV LLC.

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