Novel resist systems for EUV lithography: LER, chain-scission, nanoparticle and MORE

Brian Cardineau
University at Albany, State University of New York, bcardineau@albany.edu

The University at Albany community has made this article openly available. Please share how this access benefits you.

Follow this and additional works at: https://scholarsarchive.library.albany.edu/legacy-etd

Part of the Chemistry Commons, and the Nanoscience and Nanotechnology Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the The Graduate School at Scholars Archive. It has been accepted for inclusion in Legacy Theses & Dissertations (2009 - 2024) by an authorized administrator of Scholars Archive. Please see Terms of Use. For more information, please contact scholarsarchive@albany.edu.
Novel Resist Systems for EUV Lithography:
LER, Chain-Scission, Nanoparticle and MORE

by

Brian Cardineau

A Dissertation

Submitted to the University at Albany, State University of New York

in Partial Fulfillment of

the Requirements for the Degree of

Doctor of Philosophy

College of Nanoscale Science and Engineering

2013
Abstract

Extreme Ultraviolet (EUV) lithography is currently the best option for replacing 193-nm lithography in future IC fabrication. For EUV to be successful, however, there are a number of challenges that must be overcome. Current resist designs struggle to meet the demands of future lithography nodes. We propose the best way to overcome these obstacles is through the design of novel resist systems.

In this Thesis, we present four studies performed which were devoted to the design and understanding of EUV photoresists. Each of these four studies focused on a different area of research. Our first study, LER Limitations, was an analytical study of organic photoresists. The cause of the degradation of line-edge roughness (LER) as film thickness decreases below 90-nm was investigated as a function of substrate interaction, resist optical density, photoacid generator (PAG) attachment and glass-transition temperature (Tg). Our second study, Chain- Scission Polymers, was a synthetic study of organic photoresists. Three generations of acid- cleavable chain-scission polymers were designed, synthesized and tested. Our third study, Ligand Designs for Hafnium Nanoparticle Resists, was an analytical study of inorganic photoresists. The relative ligand-binding energies for a series of common functional groups were investigated for the binding reaction of organic ligands to hafnium-nanoparticle resists. Two series of strong binding ligands were then designed and synthesized. Our fourth study, Molecular Organometallic Resists for EUV (MORE), was a synthetic study of inorganic photoresists. Inorganic and organometallic compounds were synthesized from high EUV optical density elements and evaluated lithographically as photoresists.
Acknowledgements

I would like to thank my thesis advisor, Dr. Robert Brainard, for all the countless hours he spent teaching me. Over the years I’ve known him, he has been a boss, a teacher and a friend. I have never met anyone more enthusiastic about or more dedicated to teaching, and without his help I would never have been able to complete my research.

I would like to take this opportunity to thank my thesis committee. Through helpful conversations and research opportunities, my committee members have each help shape the content of this thesis work, and for that I am grateful.

This work would not have been possible without the contributions of many industrial researchers and funding agencies. I would like to thank SEMATECH and Intel for providing the funding for the various projects in this thesis. The staffs at the Albany AMET and Berkeley BMET have been instrumental in performing the projection-lithography experiments. Dr. Yasin Ekinci and the staff at the Paul Scherrer Institut have been very generous to this research, providing interference-lithography beam-time and support for the MORE project. I would also like to thank our project funding leaders Jacques Geroger, Karen Petrillo, Kyoungyong Cho and Ernisse Putna for helpful discussions through the years, our collaborators Dr. Christopher Ober and Dr. Emmanuel Giannelis at Cornell and Dr. Daniel Freedman and SUNY New Paltz for providing materials for this work, and Dr. Alain Diebold for assistance with and use of the Woolam-RC2 spectroscopic ellipsometer.

Finally, I would like to thank all the professors at the chemistry and nanoscale science and engineering departments of SUNY Albany who have helped in this work with helpful conversations and ideas.
Table of Contents

Abstract ........................................ ii
Acknowledgements ................................. iii
Table of Contents ................................ iv
List of Keywords ................................ vii
Dedication ......................................... viii
### Table of Contents

**Chapter I - Introduction to Photolithography and Resist Design**

1.0  Overview .................................................................................................................. 1
1.1  Introduction to Photolithography ............................................................................ 2
1.2  193-nm Photolithography ....................................................................................... 5
1.3  13.5-nm Photolithography (EUV) ........................................................................ 6
1.4  Organic Resist Designs .......................................................................................... 8
1.5  Nonconventional Inorganic Resist Designs ............................................................. 15
1.6  Resist Obstacles that Must be Overcome ............................................................... 16
1.7  Summary ............................................................................................................... 20
1.8  References ......................................................................................................... 21

**Chapter II – LER Degradation as a Function of Film Thickness**

2.0  Overview ............................................................................................................... 26
2.1  Introduction .......................................................................................................... 26
2.2  Investigations of LER Degradation ....................................................................... 29
   2.2.1  Substrate Interaction ....................................................................................... 31
   2.2.2  Optical Density .............................................................................................. 35
   2.2.3  PAG Attachment ......................................................................................... 39
   2.2.4  Glass Transition Temperature ...................................................................... 45
2.3  Summary and Conclusions .................................................................................... 51
2.4  Experimental Methods ........................................................................................ 53
2.5  References ......................................................................................................... 57

**Chapter III – Chain-Scission Polymers: Polyesters, Polyethers and Polyalkynes**

3.0  Overview ............................................................................................................... 60
3.1  Introduction .......................................................................................................... 61
3.2  Generation I – Polyesters .................................................................................... 65
3.3  Generation II – Polyethers ................................................................................... 76
3.4  Generation III – Palladium-Catalyzed Polyalkynes ............................................ 84
3.5  Summary and Conclusions ................................................................................... 92
3.6  Experimental Methods ......................................................................................... 94
3.7  References ......................................................................................................... 108
<table>
<thead>
<tr>
<th>Chapter IV – Ligand Design for Hafnium Nanoparticle Resists</th>
<th>113</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 Overview</td>
<td>113</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>113</td>
</tr>
<tr>
<td>4.2 Ligand Binding Studies</td>
<td>115</td>
</tr>
<tr>
<td>4.3 Strong Binding Free-Radical Monomer Ligands</td>
<td>122</td>
</tr>
<tr>
<td>4.4 Ligands for Aqueous Develop Nanoparticles</td>
<td>124</td>
</tr>
<tr>
<td>4.5 Lithographic Evaluations and Rethinking of Mechanism</td>
<td>126</td>
</tr>
<tr>
<td>4.6 Summary and Conclusions</td>
<td>127</td>
</tr>
<tr>
<td>4.7 Experimental Methods</td>
<td>129</td>
</tr>
<tr>
<td>4.8 References</td>
<td>134</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter V – Molecular Organometallic Resists for EUV (MORE)</th>
<th>136</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 Overview</td>
<td>136</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>137</td>
</tr>
<tr>
<td>5.2 Survey of Simple Metal Complexes</td>
<td>141</td>
</tr>
<tr>
<td>5.3 Tin Compounds</td>
<td>142</td>
</tr>
<tr>
<td>5.3.1 Sn-1 Compounds</td>
<td>143</td>
</tr>
<tr>
<td>5.3.2 Sn-12 Clusters</td>
<td>149</td>
</tr>
<tr>
<td>5.4 Metal Oxalate Complexes</td>
<td>160</td>
</tr>
<tr>
<td>5.4.1 Ligand Structure</td>
<td>161</td>
</tr>
<tr>
<td>5.4.2 Central Metal</td>
<td>162</td>
</tr>
<tr>
<td>5.4.3 Oxalate Loading</td>
<td>163</td>
</tr>
<tr>
<td>5.4.4 Optimization Studies and Champion Results</td>
<td>164</td>
</tr>
<tr>
<td>5.5 Summary and Conclusions</td>
<td>166</td>
</tr>
<tr>
<td>5.6 Experimental Methods</td>
<td>171</td>
</tr>
<tr>
<td>5.7 References</td>
<td>177</td>
</tr>
</tbody>
</table>

| Appendix – $^1$H NMR Spectra                              | 184 |
**List of Keywords**

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMET</td>
<td>Albany Micro-Exposure Tool</td>
</tr>
<tr>
<td>BMET</td>
<td>Berkeley Micro-Exposure Tool</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>Dense-lines</td>
<td>Printed lines with equal theoretical line and trench widths</td>
</tr>
<tr>
<td>Dose</td>
<td>Amount of light used in an exposure</td>
</tr>
<tr>
<td>EL</td>
<td>Ethyl Lactate</td>
</tr>
<tr>
<td>ESize</td>
<td>Dose required to print a feature with dimensions dictated by a mask</td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme Ultraviolet Lithography</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Pemeation Chromatography</td>
</tr>
<tr>
<td>HP</td>
<td>Half-Pitch (Half the size of one full repeat unit of a repeating pattern)</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
</tr>
<tr>
<td>LER</td>
<td>Line-Edge Roughness</td>
</tr>
<tr>
<td>LER Degradation</td>
<td>Degradation of LER as a function of film thickness</td>
</tr>
<tr>
<td>MORE</td>
<td>Molecular Organometallic Resists for EUV</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OD</td>
<td>Optical Density</td>
</tr>
<tr>
<td>PAB</td>
<td>Post-Applied Bake</td>
</tr>
<tr>
<td>PAG</td>
<td>Photo Acid Generator</td>
</tr>
<tr>
<td>PEB</td>
<td>Post-Exposure Bake</td>
</tr>
<tr>
<td>PMA</td>
<td>Propylene glycol Monomethyl ether Acetate</td>
</tr>
<tr>
<td>PSI</td>
<td>Paul Scherrer Institut</td>
</tr>
<tr>
<td>Resolution</td>
<td>The width of a given feature</td>
</tr>
<tr>
<td>RLS</td>
<td>Resolution, Line-edge Roughness, Sensitivity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>The amount of energy required to print a given feature</td>
</tr>
<tr>
<td>SUNY</td>
<td>State University of New York</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UL</td>
<td>Under-Layer</td>
</tr>
</tbody>
</table>
Immortality

One day my life will be over, my eyes will no longer see.
The world where I lived and loved and dreamed will go on its way without me.
Will the earth and the sky remember? Will my life leave even a trace?
Or will I be like a candle whose flame is extinguished and erased?

It's only in our daughters and sons, in our seed and breed and race,
that a spark from our soul may remain alive and continue after death.
I know nothing of hell or heaven or what comes between death and rebirth,
but I know that immortality may be found on heaven and earth.

While still I live I remember the history of my race
and my ancestors speak to me through my blood as if speaking to my face
and I speak to my sons and daughters through the mystical bonds of the flesh
and the nerves and mind of essence that make a mockery of death.

And thus will I live forever, and on to the uttermost end,
though the earth and the sky forget me as though I had never been.
I will live in my sons and daughters, in their daughters and their sons,
and when that line has come to an end I no longer wish to go on.

by Warren Cardineau
This Thesis is Dedicated to…

My loving wife, who has helped me every step of the journey.

My mother, who has supported me all my life.

My father, who I miss and wish was with us today.

My thesis advisor, who has worked countless hours helping me achieve my goals.
Chapter I

Introduction to Photolithography and Resist Design

1.0 Overview.

At the heart of every modern computer is an integrated circuit (IC), a complex network of billions of electronic switches called transistors. The first transistor was invented in 1947 by Bell Labs, but this prototype was large and cumbersome. In the late 1950’s, the integrated circuit (IC) was invented enabling chip designers to fabricate single-component systems containing multiple transistors. Chip designers found that increasing the number of transistors enabled them to make more sophisticated computers, however, these computers were large and expensive. Using photolithography, chip designers began shrinking the size of the transistor, improving computational capabilities while decreasing cost. In 1965, Intel co-founder Gordon E. Moore predicted that the IC transistor density would double every 18 months, and those predictions have become known as Moore’s Law (Figure 1.1). By following Moore’s Law, the semiconductor industry has become one of the fastest growing industries in history. As computers become smaller and faster, they enable other technologies to advance: imaging technologies allow doctors to better diagnose disease, spectroscopic equipment enable scientists to make new discoveries, and the internet supports instantaneous dissemination of information across the globe. The IC has advanced nearly every facet
of the modern world, but this advancement would not be possible without the invention of photolithography.

Figure 1.1. Moore’s law: Transistor densities will double every 18 months. Predicted in 1965, this “law” has been maintained true to today and has largely influenced the scientific, technological and medical advances of the past 50 years.

1.1 Introduction to Photolithography.

The modern IC is a complicated, multi-level circuit built in layers on a semi-conducting substrate. IC’s today are made by transferring a pattern from a mask to a photoresist using photolithography, then transferring that pattern into a substrate using etch and lastly filling-in the etched region using a deposition technique. By cycling photolithography, etch and deposition steps, multi-layer stacks of different materials are combined to form a functioning integrated circuit. All photoresists use a minimum of three processing steps: application, exposure and development.
**Application.** A solid resist film is applied to the substrate during the application step. Typically, a resist solution, consisting of the resist film solids dissolved in a casting solvent, is spin-coated on a silicon wafer, resulting in the formation of a uniform resist film. The film usually then undergoes a post-applied bake (PAB), annealing the film and removing any remaining solvent.

**Exposure.** The exposure step involves the transfer of the image from a mask onto the photoresist film. Light in the exposure tool, passes through a mask and transfers the image of the mask onto the resist. The light causes a photochemical change in the film solubility, increasing or decreasing the dissolution rate in developer. After exposure, a post-exposure bake (PEB) is frequently performed to assist in the chemical change of the exposed region.

**Development.** Part of the film is then selectively removed during development. For a *positive-tone* resist, any region of the film that was exposed to light has an *increased dissolution rate* in developing solvent. This “developer” selectively removes the exposed region producing a positive-tone image. For a *negative-tone* resist, any region of the film that was exposed to light has a *decreased dissolution rate* in developing solvent. This “developer” selectively removes the unexposed region producing a negative-tone image. (Figure 1.2)
Figure 1.2. Basic resist process flow. (1) Application of resist film by spin coating. (2) Exposure of resist through a mask. (3) Development of resist film.

The Rayleigh equation (Equation 1.1) defines the maximum resolution (R) capabilities of any optical system as a function of the numerical aperture of the optics (NA), the wavelength of light (λ), and a constant (k₁).¹² To continue increasing transistor density in modern ICs and to follow Moore’s law, the lithographic industry has used the Raleigh equation to improve resist resolution. As the transistor size has decreased from the scale of millimeters to nanometers, so too has the wavelength of light decreased from 436-nm (g-line) to 365-nm (i-line) to 248-nm (DUV). Today’s tools currently use 193-nm (ArF), but many predict 13.5-nm (EUV) lithography will be the next wavelength for lithography.¹³
\[ R = \frac{k_1 \lambda}{\text{NA}} = \frac{k_1 \lambda}{n_\lambda \sin(\alpha)} \]

**Equation 1.1.** The Rayleigh Equation. Resolution (\( R \)) is dependent on a constant (\( k_1 \)), the wavelength of illuminating light (\( \lambda \)), and the numerical aperture (\( \text{NA} \)) which is a function of the index of refraction of the medium between the optics and resist (\( n_\lambda \)) and the acceptance angle of the lens (\( \alpha \)).\(^{12}\)

**1.2 193-nm Photolithography.**

Current IC fabrication uses 193-nm immersion lithography for high resolution imaging. In 193-nm lithography, light is produced by an argon-fluoride laser source, corrected using optical lenses, and passed through a mask before it reaches the resist.\(^{10}\) As shown above, the Raleigh equation (Equation 1.1) states that improving the \( \text{NA} \) of the system can improve resolution. The \( \text{NA} \) is a function of the index of refraction (\( n_\lambda \)) of the material between the resist and the last lens of the optics. Originally this material was air, but by “immersing” the resist and optics in a fluid of higher \( n_\lambda \), the \( \text{NA} \) and thus the resolution capabilities of 193-nm lithography tools were improved without changing the source. Current 193-nm immersion scanners use water as the immersion fluid. Higher index fluids were investigated to extend the lifespan of 193-nm lithography, however, this approach has been abandoned.\(^{13}\) In order to propagate Moore’s law, the lithography industry must find an alternative to 193-nm lithography.
1.3 13.5-nm Photolithography (EUV).

Many researchers today think Extreme Ultraviolet Lithography (EUV, 13.5 nm) will replace 193-nm immersion lithography for high resolution imaging in IC fabrication. Due to the large change in wavelength of light, the transition from 193-nm to 13.5-nm lithography has caused a number of significant changes to the lithographic system. The three most challenging research areas for EUV today are the source, optics and resist chemistry, and they all need to improve in order for EUV to be successful.14

The Source. The EUV source generates radiation by plasma rather than laser emission. In 193-nm lithography, monochromatic 193-nm radiation is generated by the argon-fluoride excimer laser.15 In EUV lithography, selected elements (typically called fuel) are ionized in a high-energy plasma and the filtered emission of that plasma is used for exposure.16 This high-energy plasma is produced by either laser (LPP) or electrical discharge (DPP), causing the fuel (Li, Xe or Sn) to emit radiation. The most challenging issues facing EUV source technologies today are stability, cleanliness and above all output.

The Optics. The EUV optics must use reflective multi-layer mirrors rather than refractive lenses. In 193-nm lithography, refractive lenses are used to demagnify the mask image. In EUV lithography, the image must be demagnified through reflective multi-layer mirrors.16-18 Multi-layer stacks of
molybdenum and silicon are used in EUV lithography as Bragg reflectors to reflect the light, demagnify the image and filter out-of-band radiation. The disadvantage of using these optical systems is the efficiency. Each mirror is only ~70% reflective,\textsuperscript{19} with ~12 mirrors needed, a yield of only ~1% of the original source output is obtained. Compensation for this huge loss in output must be made by highly sensitive resists.\textsuperscript{20}

**Resist Chemistry.** The EUV exposure mechanism involves the resist interacting with electrons rather than photons. In 193-nm lithography, absorption of a photon results in the excitation of an electron from a filled-bonding orbital to an empty-antibonding orbital, resulting in a photoreaction (such as bond cleavage). In EUV lithography, photon absorption (92 eV) results in the generation of high-energy photoelectrons (typically produced by ionization of the polymer).\textsuperscript{21-26} These high-energy photoelectrons then interact with the resist to change the solubility. Two mechanisms currently exist for this interaction of photoelectrons with resists: the electron-cascade mechanism and the internal-excitation mechanism:

- **Electron-Cascade Mechanism.** In the electron-cascade mechanism, a high-energy photoelectron relaxes by ionizing the polymer, resulting in a cascade of low-energy secondary electrons and cationic holes on the polymer. Reaction of the holes\textsuperscript{21,22} or electrons\textsuperscript{23} with resist components results in the photolytic activation of the resist.

- **Internal Excitation Mechanism.** In the internal excitation mechanism, the high-energy photoelectron relaxes by interacting directly with the electrons of the resist, exciting them from a filled-bonding orbital to an empty-antibonding orbital, and simulating photon exposure.\textsuperscript{24-26}
Today, there is still debate on the dominating mechanism, and resist designers are faced with the challenge of understanding how to design resists that utilize either mechanism.

1.4 Organic Resist Designs.

Due to concerns with metal contamination by the semiconductor industry, nearly all photoresists have been based on organic polymers. Although many types of resists have been developed, all resists must have a photochemical response to light and a change in solubility as a consequence of that photochemical response.

Photochemical response. There have been many strategies used to illicit photochemical responses in resists. This photochemical response can result in the direct change in solubility of the resist film (non-chemically amplified) or it can result in the generation of a catalyst (chemically amplified) which catalytically changes solubility.

Change in solubility. Throughout the resist literature, there have been many strategies to generate a change in solubility, however these methods can be categorized in one of two ways: a change in polarity and a change in molecular weight.
• A change in polarity is coupled with the selection of developing solvent polarity to selectively develop the exposed (or unexposed) region.

• A change in molecular weight results in a significant change in dissolution rate of the film. Both chain-scission and crosslinking are common forms of molecular weight change.

Here we present an overview of the photoresist literature, by presenting five very different examples of organic resists. For each example, we will discuss what makes this resist unique, explain its mechanism and describe how it is used today.

**Figure 1.3.** Overview of the photoresist literature. Poly(methylmethacrylate) (PMMA), Poly(styrene) (PSty) and Diazonaphthaquinone (DNQ) are three examples of non-chemically amplified resists. SU-8 (commercial resist name) and Environmentally Standard Chemically-Amplified Photoresist (ESCAP) are two examples of chemically-amplified resists.
**PMMA/PSty.** Poly(methylmethacrylate) (PMMA) and poly(styrene) (PSty) are two resist polymers that undergo similar, but opposite responses. Both PMMA and PSty are non-chemically-amplified resists that undergo a change in molecular weight during exposure, however, PMMA undergoes positive-tone chain-scission\(^{28}\) while PSty undergoes negative-tone crosslinking.\(^{29,31}\)

**PMMA.** Chain-scission occurs when the polymer molecular weight is reduced by cleaving the polymer backbone, and is the dominating event in the irradiation of PMMA films. Chain-scission in PMMA results from the homolysis of the carbonyl, generating the backbone radical. This backbone radical then induces \(\beta\)-scission along the backbone, resulting in depolymerization of the chain (Figure 1.4A). Photo-induced chain-scission has been used lithographically to make positive-tone photoresists capable of 4-nm resolutions, however these resists have found more use in electron beam lithography and directed self-assembly.\(^{32}\) Ito et al. investigated modifying and improving these systems,\(^{33,35}\) however poor sensitivity and poor etch resistance are still problematic.

**Poly(styrene) (PSty).** Crosslinking occurs when the polymer molecular weight is increased by the linking of polymer chains, and is the dominating event in the irradiation of PSty films. Studies by Tabata et al. suggest that radical-cation generation, followed by radical recombination result in crosslinking (Figure 1.4B).\(^{29}\) Although these resists have been used in the
electron beam\textsuperscript{31} and nanoimprint lithographies,\textsuperscript{30} they have little use in optical lithography due to poor sensitivity and image quality.

\textbf{Figure 1.4.} Chain-Scission and Crosslinking Photoresists. (A) Homolytic cleavage of the backbone can result in depolymerization of polyacrylates.\textsuperscript{28} (B) Ionization of styrene can result in crosslinking.\textsuperscript{29}

**Diazonaphthaquinone (DNQ).** The DNQ/Novolak system is a non-chemically amplified resist system that, upon exposure, undergoes a change in solubility due to a change in polarity. DNQ is a photosensitive additive, commonly referred to as a Photo-Active Compound (PAC), which is formulated with a Novolak (polyphenol) resin and used extensively in 365-nm (i-line) lithography.\textsuperscript{36,37} Upon irradiation, the DNQ molecule liberates nitrogen and rearranges to a ketene (Figure 1.5). During alkaline development, the ketene forms the polar carboxylate salt, greatly increasing solubility in the exposed region.
Figure 1.5. Photoactive Solubility Switching Photoresists. Upon exposure, DNQ decomposes liberating nitrogen and rearranging into the ketene. The ketene is then converted into the highly soluble carboxylate in alkali developer.37

Commercial SU-8. SU-8 is a commonly used, epoxy-based negative-tone photoresist which undergoes a chemically-amplified change in molecular weight upon exposure (Figure 1.6A).38 SU-8 is a formulation containing a low molecular-weight oligomer and a PhotoAcid Generator (PAG). Upon exposure, the PAG is converted to a strong photoacid (Figure 1.6B). During the Post-Exposure Bake (PEB), the photoacid catalyzes the crosslinking of epoxide groups pendent on the oligomers (Figure 1.6C).39 Although SU-8 is used extensively to build MicroElectroMechanical Systems (MEMS), there has been little work with SU-8 as a high-resolution resist.
**Figure 1.6.** SU-8. (A) The structure of SU-8 is a mixture of oligomers. The average SU-8 segment is shown. (B) In the basic exposure, PAG is converted to a strong photoacid. (C) The photoacid from the PAG catalyzes the polymerization of the epoxides, increasing the molecular weight significantly.\(^ \text{39} \)

**Environmentally-Stable Chemically-Amplified Photoresist (ESCAP).**

ESCAP is the most highly-used class of resist in EUV today, utilizing a chemically-amplified change in polarity to change solubility. ESCAP polymers are designed with pendant, acid-labile tertiary esters bound to the polymer.\(^ \text{40–43} \) A typical ESCAP resist consists of a Photo-Acid Generator (PAG) and an ESCAP polymer. Upon exposure, the PAG is converted to a strong photoacid (Figure 1.7A). This acid catalyzes the decomposition of the pendant tertiary esters in the polymer during PEB, converting the
tertiary esters into carboxylic acids (Figure 1.7B). These carboxylic acids render the polymer soluble in 13.4 pH aqueous developer whereas the initial tertiary esters are not soluble. Resist companies such as JSR Micro Inc. have made both high resolution and high sensitivity ESCAP-type resists as shown in Figure 1.7C.\textsuperscript{44}

![Diagram showing the conversion of a tertiary ester into a carboxylic acid.]

**Figure 1.7.** Environmentally-Stable Chemically Amplified Photoresists (ESCAP) (A) Upon exposure to light, PAG is converted into a strong acid. (B) Acid-catalyzed conversion of tertiary ester to carboxylic acid on polymer.\textsuperscript{10} (C) State of the art imaging of a JSR Micro Inc. resist for 14 and 12 nm HP lines at a dose of 15 mJ/cm\textsuperscript{2}.\textsuperscript{44}
1.5 Nonconventional Inorganic Resist Designs.

Although nearly all resists to date have been based on organic polymers, there have been a few exceptions. Both silicon and hafnium-based resists have recently emerged showing great promise.

Silicon-Based Resists. Paul Scherrer Institut (PSI) has recently used a silicon-based, non-chemically-amplified resist to image 7-nm HP lines (Figure 1.8A). Hydrogen Silsesquioxane (HSQ) is a cubic silicon-oxide cluster, containing silicon at each corner, bound to one hydrogen atom and bridged by oxygen. The mechanism for HSQ involves the intermolecular metathesis reaction between a silicon-hydrogen bond of one cluster and a silicon-oxygen bond of another (Figure 1.8B). This results in a bridging between the two clusters, increasing the molecular weight through crosslinking of the film.

![Figure 1.8](image)

**Figure 1.8.** Hydrogen Silsesquioxane. (A) State of the art imaging of HSQ for 7 nm HP lines at a dose of 294 mJ/cm². (B) Exposure induces a metathesis to occur between the silicon-hydrogen bond of one cluster and the silicon-oxygen bond of another, ultimately crosslinking the film.
**Hafnium-Based Resists.** Recently, two research groups have developed photoresists based on hafnium oxide nanoparticles. The commercial resist vendor Inpria has created a completely inorganic, non-chemically-amplified nanoparticle resist with comparable resolutions to HSQ but much better sensitivity.\(^4^4\) Figures 1.9A and 1.9B show current imaging for two versions of this resist, one optimized for sensitivity, the other optimized for resolution. Cornell researchers have also designed a nanoparticle resist by forming organic-inorganic hybrid systems. These systems do not have the resolution capabilities that the Inpria resists have, but have proven to have some of the best sensitivities in lithography (Figure 1.9C).\(^4^8\)

![Image](image.png)

**Figure 1.9.** Hafnium Nanoparticle Resists. (A) Inpria/JB 12 nm HP lines at a dose of 25 mJ/cm\(^2\). (B) Inpria/IB 8 nm HP lines at a dose of 47 mJ/cm\(^2\). (C) Cornell 36 nm HP at a dose of 12 mJ/cm\(^2\).

**1.6 Resist Obstacles that Must be Overcome.**

In order for the semiconductor industry to continue to follow Moore’s Law, an alternative to 193-nm lithography must be adopted. EUV lithography is the most promising technology for the future of lithography, however there are still several obstacles that need to be addressed.
RLS Trade-Off. For EUV lithography to replace 193-nm lithography in IC fabrication, resists must show improvement in three important resist properties: resolution, line-edge roughness and sensitivity.\(^{49}\)

- **Resolution** – The dimension of a printed feature. The resolution values presented in this thesis are typically half-pitch (HP) dense-line resolutions, indicating the theoretical width of both the lines and trenches.

- **Line-edge roughness (LER)** – The average roughness of a patterned line. Calculated by measuring the deviation of a printed line from a perfect line.

- **Sensitivity** – The amount of energy (Dose) used to print a given feature.

EUV resists often show good performance with one or two of these quantities at the expense of the third. This is known as the RLS trade-off (Figure 1.10).\(^{50}\)

![RLS Trade-Off Diagram](image)

**Figure 1.10.** RLS Trade-off. It has been found that a relationship exists between resolution, line-edge roughness and sensitivity known as the RLS trade-off. It is relatively easy to improve one of these properties at expense to another, but very difficult to improve all three simultaneously for any resist.\(^{50}\)
Challenges Facing Organic Polymer Resists. Beyond the RLS tradeoff, organic polymer films are also challenged by reduction of the resist film thickness. Once developed, a resist pattern needs to be mechanically stable. If the film thickness remains constant as resolution is decreased, the patterned features will fall over (Figure 1.11). In the past, the lithography community has prevented pattern collapse by decreasing film thickness. As resolution continues to improve, the film thickness must continue to decrease, however, resist films are beginning to experience new problems which must be addressed: etch and LER degradation as a function of film thickness.

![Resolution (nm)](image)

**Figure 1.11.** Pattern Collapse. As resolution improves, film thickness needs to decrease in order to prevent pattern collapse.

Etch. For the purpose of high-resolution imaging, the ability of a resist to protect a substrate from etch is important. This has been done by selecting etch processes that etch the substrate faster than resist. As resists have gotten thinner, this selectivity is no longer sufficient to etch to the required depths. This problem has been partially overcome through the use of hard masks. A hard mask is a layer under the resist that can be etched into
using orthogonal etch processing to get deeper ultimate etch into the substrate.\textsuperscript{52,53} Hard masks present their own problems though, because they add extra steps and can cause increases in LER.

**LER Degradation as a Function of Film Thickness.** While investigating resist LER at different film thicknesses we found a LER dependence on film thickness. LER was measured for four different resists at 120, 60 and 30 nm film thicknesses. For all four resists, LER gets worse as film thickness decreases (Figure 1.12). This phenomenon is further explored in Chapter II.

![Graph](image)

**Figure 1.12.** LER as a function of film thickness for four resists; two open source resists and two resists from two different commercial vendors.
Challenges Facing Inorganic Resists. The largest challenge facing inorganic resists is preventing metal contamination in the silicon substrate. Since its inception, the lithographic industry has avoided metal-containing materials to prevent contamination of the silicon substrate. Metals can diffuse into the silicon, disrupting the semi-conducting properties and destroying the transistor. Recently, however, due to the overwhelming preliminary success of some inorganic resists, researchers are looking into how these issues can be avoided. It still remains unclear if these resists will ever be accepted by the entire semiconductor industry.

1.7 Summary.

EUV lithography remains the best option for the future of IC fabrication. In order for EUV lithography to replace 193-nm lithography, resist properties must improve. Although recent advances have been very successful, there are still huge obstacles that need to be overcome. We predict that the best way to overcome these obstacles is to invent new photoresist systems with better performance capabilities.

This thesis presents the design, synthesis and evaluation of novel photoresist materials as a means to overcome the current problems faced by EUV lithography. Chapter 2 details an investigation into the cause of the film thickness dependence on LER degradation of organic resists as discussed in section 1.6.2. Chapter 3 describes the development and synthesis of a novel chemically-amplified chain-scission organic resist platform, and
encompasses the synthesis and development of three generations of polymers.

Chapter 4 highlights collaborative work done to understand the ligand binding of the Cornell nanoparticle resists and continues with the development of new, strong-binding ligands. Lastly, Chapter 5 describes the design and development of novel inorganic and organometallic resists for EUV.

1.8 References.


3. Moore, G., Electronics (1965) 38 (8)


5. Gross, L., Nat Chem (2011) 3 (6), 493


42. Frechet, J., et al., Polymer (1983) 24 (8), 995


Chapter II

LER Degradation as a Function of Film Thickness

2.0 Overview.

Chapter II describes fundamental studies of the degradation of LER in EUV resists as a function of film thickness. The focus of this work was to better understand the LER-film thickness problem by isolating and changing different resist variables separately. Discussions of this problem with the resist community led to the study of four resist variables:

- Substrate Interaction (primed silicon vs. organic underlayer)
- Changes in Optical Density (variations in Fluorine content)
- PAG Attachment (bound and unbound)
- Glass Transition Temperature

Our experimental approach struck a balance between proprietary commercial resists and open-source resists using custom-designed polymers to address the specific variables listed above. The effect of changing each resist variable was isolated through material variation, and the resulting change in LER degradation was analyzed.

2.1 Introduction.

The need to simultaneously improve the resolution, line-edge-roughness (LER) and sensitivity of EUV resists remains one of the most critical
challenges in EUV lithography.\textsuperscript{1-4} As the resolution is improved, the resist film thickness must concomitantly decrease to prevent pattern collapse. Yet, we have found that decreasing film thickness causes degradation in LER.\textsuperscript{5}

Figure 2.1 shows the lithographic performance of four resists as a function of film thickness. These resists came from three sources (CNSE and two commercial resist vendors), yet they all show similar degradation in LER with decreasing film thickness. A more detailed study of LER vs. thickness shows that LER degrades at a rate inversely proportional to the square-root of thickness (Figure 2.2).\textsuperscript{5} Using this mathematical relationship between LER and film thickness, and assuming that the aspect ratio of the resists would remain constant at 2.4 (height/width), we predict that the LER of resist films will worsen as the International Technology Roadmap for Semiconductors (ITRS) LER goals get more demanding. We predict that if this LER degradation is not soon understood, there will be a critical gap between the ITRS goals for LER and the actual LER that can be achieved.
Figure 2.1. Lithographic performance of four resists as a function of film thickness. Es = sizing dose in mJ/cm².

Figure 2.2. (A) LER vs. film thickness for CNSE resist OS2. (B) Image study was conducted using a constant Resolution of 50 nm and appeared to be inversely proportional to the square-root of thickness. (C) Comparison between ITRS LER goals and predicted degradation of LER performance due to thin-film problem.
2.2 Investigations of LER Degradation.

To determine the resist properties that affect LER degradation in EUV resists as a function of film thickness, we studied this phenomenon as a function of resist substrate, optical density, PAG attachment and glass-transition temperature (Tg). For each of these properties, we designed a set of materials that systematically evaluate the lithographic performance of that property as a function of film thickness. We evaluated each of these material sets for film thicknesses of 90, 60, 40 and 30 nm, measured the LER for each thickness and modeled this data to evaluate the amount of change in LER as a function of film thickness.

The change in Tg as a function of film thickness is well known in the polymer literature,\textsuperscript{8-11} and has been modeled by Keddie \textit{et al.} (Equation 2.1).\textsuperscript{6} We have found that the LER response follows a similar pattern and can be modeled by a modified form of this equation (Equation 2.2). All LER \textit{vs.} Thickness and Tg \textit{vs.} Thickness plots in this chapter consist of measured data represented by points and best-fit modeled data represented by lines.

The goal of this work is to systematically change each resist variable, and evaluate the associated response to LER degradation. In order to quantify the LER degradation, we developed a protocol for measuring the area of the fit curve attributed to a change in LER which we refer to as $\varphi$. A $\varphi$ of zero represents no curvature, and thus no change in LER degradation, whereas a large $\varphi$ represents a large change in LER with changing thickness.
\[ T_g(d) = T_g \infty \left[ 1 - \left( \frac{A}{d} \right)^\delta \right] \]

**Equation 2.1.** The Keddie Model. This equation as designed to model the Tg dependence on film thickness (d), using two fitting parameters A and \( \delta \).

\[ LER(d) = LER_{\infty} \left[ 1 + \left( \frac{A'}{d} \right)^{\delta'} \right] \]

**Equation 2.2.** The LER Degradation Model. The Keddie model as adapted to fit the LER degradation data was used throughout this study.

**Figure 2.3.** Both Tg and LER change with film thickness. In this project, we defined two parameters for describing the deviation from a flat (A) Tg vs. thickness or (B) LER vs. thickness. We use the area above or under these curves, and call them \( \phi_{Tg} \) and \( \phi_{LER} \), respectively.
2.2.1 Substrate Interaction.

In 2010 we reported that the matching of the coefficient of thermal expansion (CTE) between resist and underlayer is very important in determining adhesion, line collapse and LER. Specifically, we found that the use of an underlayer can give ~20% improvement in LER over a primed silicon substrate (Figure 2.4A) and could give better LER as a function of focus vs. silicon (Figure 2.4B). We hypothesize this relationship between CTE and LER may be a result of a reduction of interfacial stress.

![Figure 2.4](image.png)

**Figure 2.4.** (A) Improvement in LER through the use of an open-source CNSE Underlayer. (B) Use of an Underlayer also improves the LER of lines as a function of focus.

As two materials with different CTEs (such as polymeric photoresists and silicon) are heated, the difference in expansion of these two materials could conceivably result in a stressed interfacial region. The stress induced in a resist film could result in non-uniform material properties ultimately causing degradation in LER. As film thickness decreases, we predict this stress would increase causing a film thickness dependent degradation in LER. An interfacial material with a CTE similar to the resist (e.g. organic underlayer) should diminish this stress, reducing the overall LER degradation.
Here we have investigated the effect of substrate (silicon vs. commercial underlayer) on the LER degradation in thin-films. Three resists from three different resist producers Company A, Company B and CNSE were evaluated on both commercial organic underlayer and primed silicon using the Albany EUV microexposure tool (AMET) at film thicknesses of 90, 60, 40 and 30 nm. LER was plotted vs. film thickness (Figure 2.5 and 2.6) and fit with the modified Keddie model (Equation 2.2) to determine $\phi_{LER}$. The area of deviation ($\phi_{LER}$) was compared for all three resists with and without underlayer. We found that there was no significant change in $\phi_{LER}$ going from silicon to underlayer (Figure 2.7). This result suggests that the LER degradation is not linked to interfacial stress.
Figure 2.5. LER vs. thickness curves and 30 nm CD SEM data for (A) Company A, (B) Company B and (C) CNSE resists on both primed silicon and organic underlayer.
Figure 2.6. SEMs of 30 nm dense line patterns for resists prepared by Company A, Company B, and CNSE on both (A) primed silicon and (B) organic underlayer.
2.2.2 Optical Density.

The Beer-Lambert law (Equation 2.3) states that the absorption of light traveling through a medium is dependent on the path length of light and the optical density of the material. The total amount of light absorption in a resist film is thus dependent on the film thickness and optical density of the film. This reduction of absorbed light could result in an increase in LER due to the statistical variation of absorbed photons (commonly referred to as shot noise). If the LER degradation is caused by reduction of light absorption, an increase in optical density for thinner films should improve the LER.
Equation 2.3. The Beer-Lambert Law. The law states that the total absorption (A) of light in a film is dependent on the optical density (OD), the path length of the light in the film (l) and the concentration of absorbing molecules (c).\textsuperscript{7}

To evaluate the dependence of LER degradation on optical density, a set of polymers with similar unexposed dissolution rates were designed and synthesized, each with varied optical density. Fluorine has a high EUV optical density and was used to increase the polymer optical densities.\textsuperscript{8} Four polymers were designed based off of the traditional ESCAP terpolymer with different levels of fluorine content (Figure 2.8). One “solubility” monomer (either the non-fluorinated 4-hydroxystyrene or the fluorinated 1,1,3,3,3-hexafluoro-2-(4-vinylphenyl)propan-2-ol) and one “non-solubility” monomer (either the non-fluorinated styrene or the fluorinated pentafluorostyrene) were chosen to cover a range of optical densities. Twelve polymers were then made varying the relative loadings of “solubility” monomer to “non-solubility” monomer, with a constant tert-butyl acrylate loading. The polymers for this study were then selected based upon a constant relative unexposed dissolution rate and optical densities were calculated for the fully formulated resists (Table 2.1).
Figure 2.8. The optical density of EUV resists was increased by preparing open-source polymers with high-fluorine content monomers.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.18</td>
<td>0.21</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>60</td>
<td>0.12</td>
<td>0.14</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>40</td>
<td>0.08</td>
<td>0.09</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>30</td>
<td>0.06</td>
<td>0.07</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>20</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 2.1. The calculated optical densities for each of the four polymers as a function of film thickness.\(^8\)

The four polymers were formulated as resists, and evaluated lithographically for film thicknesses of 90, 60, 40 and 30 nm using the Berkeley EUV microexposure tool (BMET). At each thickness, the LER of 40 and 50 nm HP lines was measured using SuMMIT,\(^9\) and the LER vs. thickness data was fit with the modified Keddie model (Figure 2.9). The LER degradation or \(\varphi_{LER}\) was then calculated for each resist and plotted against optical density of the fully formulated resists (Figure 2.10). It was found that \(\varphi_{LER}\) worsens significantly with increasing optical density, which is in direct contrast to our initial predictions.
Figure 2.9. LER vs. thickness curves and 50 nm CD SEM data for resists (A-D) prepared with varying fluorine content.
Figure 2.10. The $\varphi_{\text{LER}}$ as a function of optical density. As the film gets darker, the LER degradation gets worse.

2.2.3 PAG Attachment.

One of the most important inventions in the design of EUV photoresists has been the attachment of photoacid generators (PAGs) to polymers.$^{10-17}$ These polymer-bound PAGs are designed to improve lithographic performance by minimizing PAG segregation and diffusion length of the photo-generated acid. We reasoned that either benefit could help to improve the LER thin film problem.

**PAG Segregation.** Secondary ion mass spectroscopy (SIMS) studies have shown that fluorinated PAGs will segregate to the top surface of the resist.$^{18-23}$ Since many PAGs are dissolution rate inhibitors,$^{5,24}$ the PAG segregation to the top of the film should cause greater dissolution-rate inhibition at the film surface. We reasoned that this increase in PAG concentration at the top of the resist films would result in less top loss and thus flatter tops of the patterned lines, ultimately resulting in better LER. As resist films get thinner, less PAG would be available to accumulate at the surface, and therefore, less surface inhibition would result.
**Diffusion Length.** Several studies show minimizing acid diffusion length improves LER.\textsuperscript{25-27} Since Tg is dependent on film thickness,\textsuperscript{6,28-30} and closely related to acid diffusion,\textsuperscript{31} LER degradation in thin films may be caused by an increased diffusion of acid.

**Lithographic Evaluation vs. Film Thickness.** Our collaborators, JSR Micro Inc., specifically designed two resists for this study that differ only in the use of “blended” PAG as opposed to polymer-bound PAG. These resists were coated on organic underlayer and evaluated lithographically on the AMET at 90, 60, 40 and 30 nm film thicknesses. LER was measured and fit with the modified Keddie equation and $\varphi_{\text{LER}}$ was determined (Figures 2.11 and 2.12). For both 30 and 40 nm HP lines, $\varphi_{\text{LER}}$ improved by a factor of ~3, going from the blend to the bound PAG resists.
Figure 2.11. LER vs. thickness curves and 30 nm CD SEM data for the PAG blend and polymer bound PAG resists.

Figure 2.12. The $\varphi_{\text{LER}}$ as a function of PAG attachment. Binding the PAG to the polymer improves $\varphi_{\text{LER}}$ by a factor of $\sim 3$. 
**Cross-Sectional Analysis.** Cross-sectional analysis of the patterned lines derived from resists prepared with bound and blended PAGs was performed. The wafers were cleaved, sputtered with a thin film of palladium and gold, and evaluated in the SEM using a tilt of 10° (Figure 2.13 and 2.14).

In general, the resist prepared with the bound PAG produces much cleaner profiles than does the resist with the blended PAG, but both resists seem to exhibit residue at the base of the patterned lines near the resist-substrate interface. The bound-PAG resist exhibits clean imaging at the tops of the lines in thicker films (90 and 60 nm), yet residue in the trenches. In the thinner films, (40 and 30 nm), however, the residue in the trenches is incorporated into the top-down SEM image and top-loss of the patterned lines increases. This pattern is also true for the blended-PAG resist, however, the image degradation occurs in thicker films.

There are many possible phenomena which could contribute to the residue observed in the trenches in Figures 2.13 and 2.14 (e.g. secondary electron quenching from the substrate), we propose that the most likely mechanism concerns a decrease in catalytic activity of the photogenerated acid at the interface. We think this drop in catalytic activity could be a result from either a decrease in acid concentration or a decrease in acid diffusion rate due to Tg change.
Figure 2.13. Cross-section (left) and top-down (right) analysis of polymer-bound resist for 30 nm dense lines using a PEB of 130 °C/60 sec.
Figure 2.14. Cross-section (left) and top-down (right) analysis of polymer-blend resist for 30 nm dense lines using a PEB of 120 ºC/60 sec.
2.2.4 Glass Transition Temperature (Tg).

The Tg of polymer thin films is often dramatically different from the Tg of thick films. Figure 2.15 shows how the Tg of polystyrene decreases significantly as its film thickness drops from over 100 to 10 nm. In particular, the glass transition temperature governs several of the processes that occur during the exposure, PEB and development. Specifically, the rates of acid diffusion, base diffusion and deprotection of functional groups are likely to be strongly influenced by changes in glass transition temperature.

![Figure 2.15](image)

**Figure 2.15.** The glass transition temperature of polystyrene films, plotted as a function of thickness and fit with the Keddie model (Eqn. 1).\(^6\)

In order to systematically evaluate the dependence of LER degradation on Tg, a set of four ESCAP polymers of varied glass transition temperatures was designed. Our standard ESCAP formulation was reengineered, replacing styrene with either cyclohexyl methacrylate or hexyl acrylate, and either using
*tert*-butyl acrylate or methyladamantyl methacrylate (Figure 2.16). Each set of monomers has similar chemical structure, but very different homopolymer Tgs. By varying the composition of these polymers, a large range of resist polymer Tg was achieved (Figure 2.17).

![Figure 2.16](image1.png)

**Figure 2.16.** Variable Tg ESCAP polymers were prepared by replacing styrene with either cyclohexyl methacrylate or hexyl acrylate, and by either using *tert*-butyl acrylate or methyl adamantyl methacrylate. These monomers are chemically similar, but have drastically different homopolymer Tgs (shown under each figure).32

![Figure 2.17](image2.png)

**Figure 2.17.** Four Tg polymers (A-D) designed and synthesized with a range in Tg from 112 to 162 °C.
Glass Transition Temperature vs. Film Thickness. The glass transition temperature (Tg) is the temperature a polymer changes from a brittle to a rubbery solid. This change in material properties is attributed to polymer chains overcoming intermolecular forces in the polymer matrix. When this occurs, the slope of the thickness vs. temperature curve will change due to the free motion of polymer chains; the point at which the slope changes is taken as the glass transition temperature.

To determine the Tg of the resist films, we used spectroscopic ellipsometry (SE). SE is a technique where linearly polarized light is reflected off of a film.\textsuperscript{33-35} Through material interactions, the polarization of light is altered, generating two quantities, $\Psi$ (the amplitude component) and $\Delta$ (the phase difference). $\Psi$ and $\Delta$ measured over a range of wavelengths allows the film thickness and refractive index to be modeled with high accuracy. Using a heating stage, the film thickness measurements can be taken as a function of temperature, and from these Tg can be determined.\textsuperscript{34}

For all four resists, film thicknesses of 90, 60, 40 and 30 nm were coated and the film thickness vs. temperature curves were measured. The curves were fit with the Dalnoki-Veress model (Equation 2.4) and from this fit, the Tg was extracted.\textsuperscript{34} The Tg vs. thickness data was then fit with the Keddie model (Figure 2.18) and the $\varphi_{Tg}$ was determined.\textsuperscript{34} An overall range in Tg of 50 °C was achieved (from 112 to 162 °C).
Equation 2.4. The Dalnoki-Veress model. This model incorporates the slope of the melt (M) and glass (G) regions, the width of the Tg transition (w) and the film thickness at the Tg (c) to fit the thickness as a function of temperature curve (h(T)).

![Equation 2.4 Diagram](image)

**Figure 2.18.** Tg vs. thickness data for Tg polymers (A-D) at film thicknesses of 90, 60, 40 and 30 nm and associated $\varphi_{Tg}$ data.

**Lithographic Evaluation vs. Film Thickness.** Each resist was evaluated lithographically on the BMET at film thicknesses of 90, 60, 40 and 30 nm. The LER vs. thickness data was fit with the modified Keddie model (Figure 2.19) and $\varphi_{LER}$ was calculated.
Figure 2.19. LER vs. thickness curves and 50 nm CD SEM data for four resists of varied Tg (containing polymers A-D).

Comparing the $\varphi_{\text{LER}}$ vs. Tg curve, the LER degradation gets much worse as the resist Tg increases, and appears to go to zero when the Tg is just above the process bake temperatures (Figure 2.20). The $\varphi_{\text{Tg}}$ taken from the Tg data, seems to correlate directly with the Tg. When comparing the $\varphi_{\text{Tg}}$ with the $\varphi_{\text{LER}}$, there seems to be a direct correlation between the two, indicating
that the LER degradation is directly correlated with the Tg film thickness dependence. Due to this correlation, we think that the LER degradation is closely linked to the change in Tg.

![Graphs of LER vs. Tg, Tg vs. Tg, and LER vs. Tg](image)

**Figure 2.20.** (A) $\varphi_{\text{LER}}$ vs. Tg. The LER degradation gets worse as Tg increases, and approaches zero just above the bake temperatures. (B) $\varphi_{\text{Tg}}$ vs. Tg. The curvature of the Tg vs. film thickness curve ($\varphi_{\text{Tg}}$) seems to correlate with the Tg of the bulk material. As Tg increases, so does $\varphi_{\text{Tg}}$. (C) $\varphi_{\text{LER}}$ vs. $\varphi_{\text{Tg}}$. There appears to be a direct correlation between the degradation of LER and the Tg thickness dependence.
2.3 Summary and Conclusions.

The effect each of four variables has on the LER degradation as a function of film thickness in EUV photoresists has been investigated. Figure 2.21 shows all four variables plotted together, resulting in the most significant effects from the PAG attachment and Tg studies. These results suggest a change in film properties near the interface, resulting in a change in acid diffusion length.

![Graph showing LER degradation](image)

**Figure 2.21.** Side-by-side comparison of LER degradation ($\phi_{\text{LER}}$) across four studies: substrate interaction, optical density, PAG attachment and glass transition temperature.

**Substrate Interaction.** We investigated the effect on LER degradation of substrate physical properties by evaluating three resists from different vendors on both primed silicon and organic underlayer. Very little change in LER degradation due to substrate composition was observed. We had originally hypothesized that stress induced in the film by a mismatch of CTE could cause this thickness-dependent LER degradation. Since there was no observed correlation between substrate and LER degradation, the physical properties of the interfacial materials do not cause LER degradation.
**Optical Density.** We investigated the effect on LER degradation of optical density by evaluating four resists containing polymers with different optical densities. A series of resist polymers were synthesized, varying the optical density by changing the fluorine loading. Lithographic evaluation of these resists resulted in the opposite of the predicted effect, as optical density increased, LER degradation became worse. We hypothesize the worsening of LER degradation is a result of a change in morphology of the film. As the fluorine content of the polymer increases, the segments of the polymer become more hydrophobic. This change in hydrophobicity may cause partial phase-segregation of the polymer, resulting in a change in physical properties (i.e. diffusivity, Tg) and the possible formation of mesoscale polymer structure.

**PAG Attachment.** We investigated the effect on LER degradation of PAG attachment by evaluating two resists which varied only in PAG attachment. Our collaborators, JSR Micro Inc., specifically designed two resists for this study that differ only in the use of “blended” PAG as opposed to polymer-bound PAG. The resist containing a bound PAG had a ~3 fold improvement in LER degradation over the PAG blend. Furthermore, cross-sectional SEM analysis indicated the LER degradation occurs near the wafer interface, and is incorporated in the SEM image only when the film thickness is thin enough. We hypothesize that this region of degraded image quality is a result of a change in the physical properties of the film near the interface.
Glass Transition Temperature (Tg). We investigated the effect on LER degradation of the glass transition temperature by evaluating four resists with similar chemical structures but varying Tg. Both the LER and Tg were measured for each resist as a function of film thickness, and the LER degradation was found to directly correlate with the change in the Tg curve. We hypothesize this correlation, along with the results from the PAG attachment study, supports a mechanism of an interfacial region of decreased Tg near the wafer surface. If the Tg near the interface is lower than the remaining film, acid diffusion would be greater near the interface, resulting in a region of degraded LER. As the film thickness decreases, this degraded LER region is incorporated into the SEM image, resulting in an increase in the measured LER. In the bound-PAG system, acid-diffusion is controlled due to polymer bulk thus minimizing this region of degraded LER.

2.4 Experimental Methods.

Materials. Unless otherwise specified, all starting materials for polymer synthesis were purchased from Sigma Aldrich. 1,2,3,4,5-pentafluoro-6-vinylbenzene, and 1,1,1,3,3,3- hexafluoro-2-(4-vinylphenyl)propan-2-ol were provided by Central Glass to make polymers for the optical density study. Bis(3-tertbutylphenyl)iodonium nonaflate PAG was provided to us by Toyo Gosei for use in both optical density and Tg studies. Methyl adamantyl methacrylate was provided by Company B for use in the Tg study.
Polymerization of polymers for Optical Density and Tg Studies. A modified form of the method described in US Patent 6,042,997. The appropriate ratios of three monomers (10.8 total mmol used) were dissolved in isopropyl alcohol (16 mL). Nitrogen was bubbled through the reaction mixture for 10 minutes. The solution was heated under reflux. Once the reflux temperature was reached, azoisobutynitrile (AIBN) (0.043 g, 0.26 mmol) was added to the solution in one portion. The mixture was then stirred at reflux for 16 hours. Ammonium acetate 0.56 g, 7.3 mmol) dissolved in water (1 mL) was added to the mixture. Heating at reflux was continued for 16 hours. The mixture was then cooled to room temperature and added dropwise to water (100 ml), the slurry was filtered. The resulting solid was triturated with methylene chloride (100 ml) stirred for 30 minutes than filtered. The solid was dried under vacuum.

Lithographic Process Conditions for Substrate Interaction Study. Company A resist A, Company B resist B and CNSE resist “OS5” were all run at the Albany EUV MET (AMET). The two substrates used were either HMDS-primed silicon or a commercial organic underlayer. The resists were coated to the appropriate thickness on the appropriate substrate, baked for appropriate PAB (Table 2.2), exposed, baked for appropriate PEB (Table 2.2) and developed for 60 sec. using a standard MF CD-26 developer. Metrology was then performed using Albany CD SEM.
Lithographic Process Conditions for Optical Density and Tg Studies.

All resists in these studies were lithographically evaluated at Lawrence Berkeley National Laboratories using the Sematech EUV Microexposure Tool (BMET). The resists were coated to the appropriate thickness on HMDS primed silicon, a PAB of 130 °C for 60 sec was used, the resists were exposed, a PEB of 110 °C for 90 sec was used and the resists were then developed for 60 sec using a 0.26 N tetramethylammonium hydroxide (TMAH) developer. Metrology was performed using a Hitachi 4800 SEM with a working distance of 4 mm and a magnification of 150K X. LER measurements were taken using SuMMIT at the best focus, close to sizing dose.9

Lithographic Process Conditions for Substrate Interaction and PAG Attachment Studies. All resists in these studies were lithographically
evaluated at the Albany College of Nanoscale Science and Engineering facility using the Sematech EUV Microexposure Tool (AMET). The resists were coated to the appropriate thickness on a commercial organic underlayer, a PAB of 130 °C for 60 sec was used, the resists were exposed, a PEB of 120 °C for 60 sec (the bound PAG resist was found to be too slow and so was done at a PEB of 130 °C for 60 sec) and the resists were then developed for 60 sec using a 0.26 N tetramethylammonium hydroxide (TMAH) developer. Metrology was then performed using a CD SEM.

**Measurement of Glass Transition Temperature.** For all Tg measurements, resist films were coated to the appropriate film thickness on a silicon wafer and soft baked at 130 °C for 60 sec. The wafer was then placed on a Woolam RC2 spectroscopic ellipsometer equipped with a heating stage. The films were subject to an initial heating from 30 to 160 °C over 20 mins to allow residual solvent to outgas. Film thickness vs. temperature measurements were then taken on cooling from 160 to 30 °C over an additional 20 mins, using a standard Cauchy data fit. The thickness vs. temperature data was then fit to the Dalnoki-Veress equation and from that fit, the Tg was extracted.

**Error Calculations for φ.** The error in φ was calculated by adding or subtracting the error for each point and fitting this data to the modified Keddie equation, resulting in an overestimate and an underestimate of φ. The error of φ was then taken as half the difference in either direction (Figure 2.22).
Figure 2.22 The error in $\varphi$ was determined by overestimating and underestimating $\varphi$ and taking half that difference as the error in either direction.

2.5 References.


8. Optical densities calculated for formulations containing 15% bis(4-tert-butylphenyl)iodonium nonaflate PAG and 1.5% tetrabutylammonium lactate base using the CXRO Henke Filter Transmission.

9. SuMMIT is a software package provided by the lithometrix company and is the standard method for analysis of imaged SEM data.


15. Wu, H., University of Connecticut, Storrs, CT, 2001
32. Poly(methyl adamantly methacrylate) homopolymer Tg was modeled using Bicerano Tg model – “Prediction of Polymer Properties – Third Edition, Revised and Expanded"


Chapter III

Chain-Scission Polymers: Polyesters, Polyethers and Polyalkynes

3.0 Overview.

Chapter III focuses on the development of novel photoresist materials based on acid-cleavable chain-scission polymers. The goal of this work was to create chain-scission resist polymers containing acid-cleavable functionalities in the backbone. Upon exposure to photo-generated acid, polymer chain-scission should occur, combining the high-resolution capabilities of PMMA resists with the excellent-sensitivities of ESCAP resists. Over the course of this work, we synthesized and lithographically evaluated three generations of chain-scission polymers. For each generation, monomers and polymerization techniques were developed and polymers were lithographically evaluated. An overview of the three generations is listed below.

- Generation I polymers were made by the polyesterification reaction of acid-cleavable diols and diacyl chlorides.
- Generation II polymers were made by the polyether condensation reaction of acid-cleavable α-chloroesters and di(hydroxy)aromatic linkers.
- Generation III polymers were made by the palladium-catalyzed polycoupling reaction between an acid-cleavable di(trimethylsilylalkyne) and a dihalobenzene.
3.1 Introduction.

As stated in section 1.6.1, resolution, LER and sensitivity need to simultaneously improve in order for EUV lithography to be successful, however, one or two these properties often improves at the expense of the third and this is known as the RLS trade-off.\(^1\) We propose that novel chain-scission polymers can improve all three properties simultaneously. Chain-scission polymers undergo backbone cleavage during the photolithographic process through ionizing radiation, electron beam exposure and recently, acid catalysis. Cleaving the main-chain results in a reduction of polymer molecular weight which subsequently changes many of the film properties such as increasing the dissolution rate and decreasing the Tg. Furthermore, the resolution capabilities of chain-scission polymers are typically much better than other polymeric systems due to the cleaving of individual polymer chains.

The polymethylmethacrylate (PMMA) resist is a key example of the excellent resolutions achievable by chain-scission (Section 1.4.1).\(^2-7\) This resist undergoes chain-scission both through ionizing radiation and electron beam exposures. Despite some compelling advantages, PMMA resists have a number of drawbacks that have prevented their widespread use, such as the need for organic solvent development, high outgassing, poor etch resistance and poor sensitivity. Other important work in this area has included optimized PMMA-type polymers,\(^8\) polyacetsals,\(^9,10\) self-developing polymers,\(^11\) and non-chemically amplified polycarbonates (Figure 1).\(^12\) Despite continuing research in these areas, organic solvent development, high outgassing levels, and achieving high molecular weights during polymerization continue to hinder the success of these systems.
Figure 3.1. Examples of chain-scission polymers: Polycetals, PMMA, optimized PMMA-type, Chemically-Amplified Self-Developing, Non-Chemically-Amplified Polycarbonate.

Here, we describe the synthesis and lithographic evaluation of a new chain-scission resist- type based on the acid-catalyzed cleavage of tertiary or secondary-activated esters. Through this system, we predict the acid cleavable functionality of the ESCAP resist can be combined with the chain-scission capabilities of the PMMA resist to simultaneously improve upon the resolution, LER and sensitivity of other EUV resist systems.

**Improved LER due to the scission of polymer chains.** In a traditional chemically- amplified resist, whole-polymer segments develop out of the polymer matrix, resulting in a line-edge defined by polymer constituents. Since the radius of gyration of a resist polymer is typically ~1 to 5 nm, the theoretical limitations of LER are dictated by the polymer size. In chain-scission polymers, the acid cuts through the polymer chains, enabling the line-edge to be composed of polymer fractions and so the
theoretical limitations of LER are not dependent on entire polymer size but rather on the size of the smallest cleavable segment.

**Improved Sensitivity due to an increase in exposed region diffusivity.**

In the exposed region, acid catalyzes the breakdown of the polymer molecular weight. We predict this decrease in molecular weight will result in a decrease in the Tg of the exposed region and thus an increase in diffusivity.\textsuperscript{15-17} An increase in diffusivity in the exposed region should allow the acid to move more freely within the exposed region and catalyze more of the polymer cleavage, decreasing the total amount of acid needed and improving the sensitivity.

In order for these resist systems to function efficiently, we have developed three design criteria which we predict will improve the probability of success of these systems. The polymers must have: acid-labile functionality in the backbone, baseline solubility control and molecular weight control.

**Design Criteria 1: Acid-labile functionality in the backbone.** In order for these polymers to undergo chain-scission, acid-labile functionalities must be incorporated into the backbone (Figure 3.2). To do this, step-growth monomers must be made which contain polymerizing functionalities on either side of an acid-labile functionality. Examples of acid-labile functionalities discussed in this chapter are: tertiary esters and secondary allylic esters.
Figure 3.2. Tertiary and secondary allylic ester linkages. (P) = polymer linkage.

**Design Criteria 2: Baseline solubility control.** After exposure, a resist polymer must become soluble during develop (for a positive-tone resist). By making the polymer partially soluble in developer (baseline solubility), less work must be done during exposure to promote dissolution.

**Design Criteria 3: Molecular weight control.** In order to achieve the greatest benefit from chain-scission and optimize the system for molecular weight, a wide range of polymer molecular weights must be achievable. Our synthetic goal range is 5 to 20 kDa polymers.

Through the work in this chapter, we plan to address a number of questions we have developed about acid-cleavable chain-scission polymers:

- Can acid-cleavable polymers be made and how do they function as resists?
- How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists?
- Can high Tg, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?
3.2 Generation I – Polyesters.

Here we present our first series of chain-scission polymers made by the polyesterification reaction between cleavable diols and di(acid chloride) linkers which we have named Generation I - Polyesters. Here we present a series of monomers containing two cleavable diols (CD1 and CD2) and two di(acid chloride) linkers (IPC and AIC) which were reacted together to produce Generation I polymers (Figure 3.3). In this section we will describe the synthesis of these monomers, the synthesis of a series of Generation I polymers, and the overall lithographic evaluation of this system.

![Cleavable Diols and Di(acid chloride) Linkers](image)

**Figure 3.3.** Generation I monomers set. Two cleavable diols (secondary allylic CD1 and tertiary CD2) and two di(acid chloride) linkers (with added solubility AIC and without IPC) were designed and synthesized.
Cleavable Diols. Our strategy for making Generation I polymers is to react cleavable diols (CD1 and CD2) with di(acid chloride) linkers (IPC and AIC) in a polyesterification reaction (Figures 3.3 and 3.4). Cleavable diol 1 (CD1) is a commercially available secondary allylic diol and can be used directly in the polymerization reaction due to the relatively low steric inhibition of the secondary alcohol. Our attempts to polymerize tertiary diol (1) directly failed likely due to steric inhibition. Cleavable diol 2 (CD2) was designed such that two acid labile tertiary esters are bound between two primary alcohols. The primary alcohols are important due to their low steric inhibition and thus high reactivity towards polymerization. CD2 was prepared by reacting the tertiary diol (1) with chloroacetic anhydride yielding the di(α-chloroester) (2). The reaction of 2 with triethylammonium formate, followed by hydrolysis, yields CD2 (Figure 3.6).

![Chemical Structure](image)

**Figure 3.4.** General scheme for polyester synthesis.

![Chemical Structure](image)

**Figure 3.5.** Synthesis of tertiary cleavable diol CD2.
**Di(acid chloride) Linkers.** As mentioned in **Design Criteria 2**, control over the baseline solubility of the polymer is important and can be achieved through the development of two di(acid chloride) linkers: IPC and AIC. IPC is commercially available, and was recrystallized from hexane before use. AIC was synthesized by protecting the hydroxyl group of compound 3 using acetic anhydride followed by converting the two carboxylic acid groups into acid chlorides using the Vilsmeier’s reagent (Figure 3.6).\(^{18,19}\) AIC was then fractionally distilled at 180 °C under high vacuum and crystallized to ensure purity.

![Synthesis of di(acid chloride) linker AIC](image)

**Figure 3.6.** Synthesis of di(acid chloride) linker AIC.

**Developing Polymerization Conditions.** One of the challenges in synthesizing step-growth polymers is producing them with a high molecular weight. Polyester condensations are traditionally performed on large scales at elevated temperatures such that one monomer is slowly distilled, driving the stoichiometry to equivalence.\(^{20}\) To obtain polyesters with a high molecular weight under other conditions, precise control over stoichiometry is critical. Even low levels of impurities can dramatically reduce the molecular weight.\(^{21}\) Our polymers were synthesized on a small scale, under anhydrous conditions, and at relatively low temperatures. Low temperature synthesis was required to
prevent the inadvertent cleavage of the tertiary or secondary allylic ester groups.

In our initial experiments, we had difficulty preparing polymers with Mw greater than 3,000-5,000 kDa. This is likely due to the formation of macrocycles (Figure 3.7). If the solvent does not properly solvate the polymer segment, the polymer can ball up, putting reactive chain-ends in close proximity to each other and allowing them to react forming a macrocycle. If macrocycle formation occurs, one additional scission is needed to open the macrocycle before molecular weight is reduced. Furthermore, design criteria 3 states control over molecular weight is necessary. In order to prevent macrocycle formation we tested a series of solvents to find one that properly solvates the growing polymers. We found pyridines form polymers with molecular weights greater than 20 kDa, and were used throughout this study (Table 3.1).

![Figure 3.7. Macrocycle formation. A) A properly solvated polymer segment has separation between reactive chain-ends. B) A poorly solvated polymer segment where reactive chain-ends are folded together, resulting in macrocycle formation.](image)
Table 3.1. Solvents tried and molecular weights achieved. Study performed on one equivalent of CD1 and one equivalent AIC.

Deprotection Kinetics. AIC was synthesized as a means of providing our polymers with some baseline solubility. We hypothesize that polymers with some initial solubility in developer will require less polymer cleavage to become completely soluble, and therefore, will require less dose during exposure. In order to get this benefit, however, polymers containing AIC need to be deprotected. As this deprotection reaction must occur in the presence of several backbone esters in our polyester polymers (Figure 3.8A), understanding the kinetics and selectivity of this deprotection reaction is crucial. Because the peaks in the $^1$H nuclear magnetic resonance (NMR) spectra of polymers tend to be too broad for detailed kinetic studies, we designed and synthesized a small molecule with five representative ester linkages to model this critical deprotection reaction (Figure 3.8B).
Figure 3.8. CD2-AIC Copolymer (A) and the pentaester deprotection kinetics model (B).

We studied the kinetics of the deprotection reaction of the model pentaester with ammonium hydroxide using NMR. After exploring different deprotection conditions, a 0.1 N solution of ammonia in d₆-dimethylsulfoxide and d₄-methanol was found to give use the best results. As we ran the kinetics, we observed that the acetate peak located at δ 2.26 ppm (Figure 3.9, peak A) shifted upfield and split into δ 1.93 ppm and δ 1.82 ppm (Figure 3.9, peaks B). These peaks are likely to correspond with the formation of acetamide and acetic acid. Figure 3.10 shows the overall deprotection rate of the phenolic polymer in the pentaester model compound.
Figure 3.9. NMR shift of the phenol acetate peak of model compound during NMR kinetics study.

Figure 3.10. Results of NMR kinetics study.

**Lithographic Evaluation of Generation I Polymers.** Six polyester chain-scission polymers were synthesized and evaluated lithographically. Polymers were prepared from two diols (CD1, CD2) and varied ratios of the two di(acid chloride) linkers (IPC, AIC) (Table 3.2). Polymer A (IPC/CD2) was not soluble in standard resist solvents, and so was not
lithographically evaluated. The other five polymers were formulated with PAG and base, and imaged at the BMET.

<table>
<thead>
<tr>
<th>% Phenolic Monomer</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPC</td>
<td>0</td>
<td>IPC/CD2 (50/50)</td>
<td>IPC/AIC/CD2 (25/25/50)</td>
<td>IPC/CD1 (50/50)</td>
<td>IPC/AIC/CD1 (25/25/50)</td>
<td>AIC/CD1 (50/50)</td>
</tr>
<tr>
<td>1:1 Mixture of IPC and AIC</td>
<td>25</td>
<td>IPC/AIC/CD2 (25/25/50)</td>
<td>AIC/CD2 (50/50)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AIC</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.2.** The synthesis of six chain-scission polymers (A through F) varying cleavable monomer and baseline solubility (IPC vs. AIC).

The resists prepared from polymers B and C (IPC/AIC/CD2 and AIC/CD2) gave similar imaging results with a PEB of 110 °C/60 sec (Figure 3.11). Both resists appeared overexposed at 3 mJ/cm² and the entire area close to the exposed region appears to have liquefied. When polymer C was rerun at a lower PEB (70 °C/60 sec), imaging was obtained, although image quality is poor below 80 nm HP (Figure 3.12).
Figure 3.11. Light microscope imaging of resists containing polymers B and C. The exposure appears to have completely liquefied the exposed region along with its surrounding regions.

Figure 3.12. Dense-line images of resist prepared from Polymer C (AIC/CD2, 50/50) with a PEB = 70 °C/60 sec.

Resists prepared from polymers D and E (IPC/CD1 and IPC/AIC/CD1) resolved ~100 nm dense lines at a dose of 32 and 16 mJ/cm², respectively (Figure 3.13). Although the resolution capability of these resists is poor, they demonstrate that adding baseline solubility is important to increase sensitivity. As the amount of AIC is increased from 0 % (polymer D) to 25 % (polymer E),
the sensitivity improves by a factor of 2X. The resist prepared with polymer F (AIC/CD1) gives the best overall imaging. This resist is capable of resolving ~30 nm dense lines at a dose of 20 mJ/cm².

Figure 3.13. Dense-line images of resist prepared from Polymer F (AIC/CD1, 50/50): 40, 36, 32, and 28 nm half-pitch at a dose of 22.5 mJ/cm².

Although these Generation I resists showed very hopeful preliminary imaging, subsequent lithographic evaluation showed inconsistency in performance and image quality. Figure 3.14 shows a subsequent imaging result of polymer F. This is a low-magnification SEM image of patterned lines where the patterned regions appear to have peeled off of the wafer. We hypothesize these inconsistencies are due to variations in the polymer chain ends which can be attributed to the reactivity of the acid chloride functionality.
**Figure 3.14.** Reproducibility issues with polymer F. Polymer F was found to have reproducibility issues which may be due to monomer reactivity.

**Analysis of Results.** Acid chloride functional groups are known to be very reactive intermediates and may have resulted in inconsistent polymer properties. We predict the di(acid chloride) linkers could have formed:

- Polar acyliuminium salts by reaction with pyridine.
- Polar carboxylic acids by reaction with water.
- Non-polar arylchlorides by loss of carbon monoxide.

If even a small percent of these side products formed on the chain ends, the polymer morphology could change significantly. Conceivably, if the polar (or non-polar) side groups caused the polymer film to form mesoscale pockets of polar (or non-polar) regions, this could have significant effects on the acid diffusion, mechanical properties, dissolution rate and glass transition
temperature (Tg) of the film. Thus a seemingly minor change in the polymer could result in dramatic changes to the image quality.

**Figure 3.15.** Possible side products formed at chain-ends. It is conceivable that the highly reactive acid chloride chain ends could result in side-production of 1) acyliminium salts 2) carboxylic acids 3) arylchlorides. This change could have dramatic effects on the resist physical properties.

### 3.3 Generation II – Polyethers.

We hypothesize the reproducibility issues of Generation I are linked to acid chloride reactivity, so in Generation II the highly reactive acid chloride was replaced with a less reactive α-chloroester. Here, we present a new series of acid-catalyzed chain-scission polymers, made by the polyether condensation reaction of a diol and a di(α-chloroester). The α-chloroester functional group is much less reactive than the acid chloride, thus allowing the chain-scission polymer to be made with greater control over side reactions. In the following section, we will describe the synthesis and preliminary evaluation of a series of acid-catalyzed chain-scission polymers made through this polyether condensation reaction.
Cleavable Monomers. A series of three cleavable monomers containing α-chloroester functional groups was designed and synthesized. For this polymer system to cleave, it is important to incorporate cleavable functionalities into the backbone of the polymer chains. All cleavable monomers were designed with α-chloroester functional groups on either side of an acid-cleavable moiety. In order to have a range in reactivity of the cleavable polymers, tertiary aliphatic (CM1), and benzylic (CM2, CM3) esters were developed into monomers (Figure 3.16). Furthermore, to improve alkaline developer solubility, CM3 was designed with a protected phenol group.

![Monomers CM1, CM2, CM3](image)

**Figure 3.16.** Three Cleavable Monomers made, each containing acid-cleavable functionalities between two α-chloroester functional groups.

The most difficult step in the synthesis of these monomers was the formation of the tertiary ester. Chloroacetyl chloride and anhydride both readily undergo elimination to form the ketene under basic conditions,\(^2\) however our product is acid labile and can easily eliminate under acidic conditions. Monomer CM1 was made during Generation I by heating the appropriate diol in dilute hexane with chloroacetic anhydride. Monomers
CM2 and CM3 however, underwent acid-catalyzed elimination under these conditions. The successful synthesis of CM2 and CM3 was ultimately accomplished by the dicyclohexylcarbodiimide (DCC) coupling of the activated tertiary esters with chloroacetic acid (Figure 3.17).²⁴

![Chemical reactions](image)

**Figure 3.17.** The more stable aliphatic CM1 was made under acidic conditions however, the more reactive benzylic CM2 and CM3 eliminated. These more reactive monomers were made by DCC coupling.²⁴
**Di(hydroxy)aromatic Linkers.** There were two di(hydroxy)aromatic linkers used in this study. In order to form polymers, a nucleophilic functionality is needed to react with the α-chloroester of the cleavable monomers in S_N2 fashion. Phenol is a good nucleophile, it can be deprotonated under mild conditions and has a good etch resistance, so for these reasons, we designed phenol linkers for Generation II. Two diphenol compounds were selected for use as monomers: BPA and TBE (Figure 3.18). As stated in Design Criteria 2, it is important to control the baseline developer solubility of the polymer. TBE was designed to increase solubility of the cleaved polymer segments in alkaline developer, while the commercially available BPA was added to further improve etch resistance.

![BPA and TBE](image)

**Figure 3.18.** Two diphenol linkers, BPA and TBE. BPA is a commercially available linker which should increase etch resistance of the polymer film. TBE was designed to cleave under exposure and add solubility to exposed polymer fragments.

**Developing Polymerization Conditions.** Due to the relative stability of the α-chloroester functional group, investigation of the polymerization conditions was necessary. Initial attempts at polymer synthesis involved phase-transfer reactions, but this resulted in oligomer precipitation (~1 KDa). Combining reagents in N,N’-dimethylformamide (DMF) with sodium carbonate
improved the molecular weight slightly (~2 KDa), but the reaction was slow. When these reagents were heated, however, the clear solution became dark red and no products were recovered. Since this reaction was not deoxygenated, we think the dark color that formed was due to oxidation of the phenol monomer. After the solution was thoroughly degassed, moderate molecular weights were achieved (5 – 10 KDa).

**Lithographic Evaluation of Generation II Polymers.** As a preliminary evaluation of this system of resists, two polymers were synthesized and evaluated lithographically for EUV sensitivity. Polymer G was made with tertiary aliphatic cleavable groups (CM1) while Polymer H was made with tertiary benzylic cleavable groups (CM2 and CM3) as described in Table 3.3. Both polymers were formulated with PAG and base and imaged using the EUV microexposure tool at Lawrence Berkeley National Laboratories (BMET).
Table 3.3. The monomer compositions of two polyether polymers G and H.

![Table 3.3. The monomer compositions of two polyether polymers G and H.](image)

After exposure, polymer G formed a visible latent image; however no dissolution contrast was obtained and the patterns were not visible by SEM (Figure 3.19A). Polymer H, however, showed promising imaging, with modulation down to 14 nm HP (Figure 3.19B). We think this preliminary imaging shows the high resolution capabilities of these chain-scission resist systems, however, this polymer type may have problems with Tg and hydrophobicity.
Figure 3.19. Two polymers were tested for imaging. (A) Image is visible by light microscope, but not by SEM which we believe is due to no dissolution contrast. (B) Capable of resolving larger patterns and modulating down to 14 nm HP.

Analysis of Results. Clearly, the image quality of the patterned features in figure 3.19B is poor below 40 nm HP. The patterns appear to have severe pattern collapse and a significant amount of bridging. We think both of these issues are due to the high ether content of polymer H.

Pattern Collapse. One explanation for the severe pattern collapse is a Tg of the patterned lines below room temperature. When the Tg is below the temperature of a polymeric material, the material is said to be in the “rubber region”. The “rubber region” is a result of the free energy of individual polymer chains exceeding the intermolecular forces, allowing the free-motion of individual chains. On the macro-scale, the physical properties of the polymer are flexible and malleable. Under most circumstances, the Tg is dictated by the chemical structure of the polymer and does not change, however, there is a physical phenomenon that exists in thin films causing the Tg to decrease as a
function of film thickness. As the thickness of polystyrene films on silicon substrates decrease from 100 nm down to 10 nm, the Tgs of these films decrease by over 30 °C.\textsuperscript{31} Furthermore, free-standing polystyrene films have been shown to decrease at twice the rate of films on a silicon substrate.\textsuperscript{32} As we showed in section 2.2.4, photoresist films follow a similar trend to polystyrene. We predict the Tg of a patterned-line decreases significantly due to a change in film thickness, both perpendicular to and in the plane of the wafer. When a line is patterned, the line can be thought of as a free-standing film. The Tg of this free-standing line should decrease due to the film thickness perpendicular to the wafer and, depending on the resolution, it should also decrease as a free-standing film. Figure 3.20 shows the imaging for 50-nm HP lines and 20-nm HP lines for polymer H. The 50-nm lines appear to be rigid, with a Tg above room temperature and no pattern collapse. The 20-nm lines appear to be flexible and to have experienced severe pattern collapse. Using the Bicerano Tg model we predict the Tg of polymer H to be 60 °C, and we reason the pattern collapse in the 20-nm lines is a result of the Tg dropping below room temperature.
Figure 3.20. The Tg is already very low, if it were to drop much lower it might drop below room temperature, resulting in significant change in mechanical properties.

Bridging. One explanation for the bridging is polymer swelling (Figure 3.21). During development, water can diffuse into the patterned lines, resulting in swelling. If the lines swell until they touch, the lines can stick to each other and form bridges. The amount of swelling is primarily dependent upon the hydrophilicity of the polymer. Poly(ethers), such as poly(ethylene glycol) (PEG), are used in biomedical applications for their high swelling ability. With the high ether content of polymer H, it is conceivably that the lines swelled to the point of touching and stuck to each other, causing bridging.
Figure 3.21. Bridging of patterned lines. As the patterned lines swell in developer, if they touch they can bond to each other. After drying, this bond would remain as a bridge.

3.4 Generation III – Palladium-Catalyzed Polyalkynes.

To correct for the Tg and hydrophobicity problems of Generation II, Generation III was developed. Here, we present a new series of acid-catalyzed chain-scission polymers, made by the palladium-catalyzed hiyama coupling reaction of acid cleavable di(trimethylsilylalkyne)s and di(iodo)aromatic linkers. These functional groups are stable under standard conditions, preventing side product formation and the predicted Tg and hydrophobicity should be significantly higher than polyethers. In this section, we will describe the synthesis and preliminary studies of acid-catalyzed chain-scission polymers made through this palladium- catalyzed polyalkyne reaction.

Prediction of Tg and Hydrophobicity. While designing this series of polymers, it was helpful to model the properties of the polyalkynes to ensure the properties were being improved. We used the Bicerano Tg model to model the Tg of two similar polymers; one generation II and one generation III
Due to the rigidity of the alkyne groups, we predict the Tg to be much higher (115 °C) than with a similar generation II polymer (-5 °C). Furthermore, the generation II polymer has a 3:1 carbon to oxygen ration whereas the generation III has a much higher carbon content of 5:1. We predict the 35% reduction of hydrogen-bonding oxygen should result in a better hydrophobicity and less swelling.

**Figure 3.22. The predicted Tg of two polymers.** The Bicerano model predicts the Tg of generation III polymers can be 120 °C higher than similar generation II polymers.\

**Hiyama Catalytic Cycle.** Hiyama coupling is one of many palladium-catalyzed reactions where an alkyl halide is coupled to an activated nucleophilic carbon, forming the C-C bond. In the Hiyama coupling reactions that will be discussed in this section, the reaction starts with the activation of a silyl alkyne. Fluoride has a high affinity for silicon and, when combined with a trimethylsilylalkyne, reacts to form the silyl anion (Figure 3.23). This step is fast and usually occurs first. During the catalytic reaction cycle, the Pd(0) complex undergoes oxidative addition with an aromatic iodide to form the activated organo-Pd(II) complex (Figure 3.23A). This activated organo-Pd(II) complex undergoes a transmetallation reaction with the silyl-anion complex.
formed earlier, resulting in the formation of the diorgano-Pd(II) complex (Figure 3.23B). Finally, the diorgano-Pd(II) complex undergoes reductive elimination to form the coupled product and the recycled catalyst (Figure 3.23C).

**Figure 3.23.** Catalytic cycle for the Hiyama coupling reactions discussed in this chapter.

**Cleavable Di(trimethylsilylalkyne)s.** To test the viability of these generation III polymers, our initial goal was to synthesize and characterize a single polymer made from a cleavable monomer. The Hiyama reaction involves the coupling of an aromatic halide with an activated silyl alkyne (or variations). In order to make the chain-scission polymer from this coupling method, tertiary esters were designed between trimethylsilylalkynes, as shown in figure 3.24. CA1 was made by the addition of trimethylsilylpropynoyl chloride to the dilithium salt of tertiary diol 1.37
Figure 3.24. Generation III monomer CA1 was made by adding trimethylsilylpropynoyl chloride to the diliithium salt of tertiary diol 1.

Di(iodo)aromatic Linkers. Four di(iodo)aromatic linkers were made for this study, DL0 through DL3. To incorporate baseline solubility, two monomers were designed: with (20) and without (DL0) phenol (Figure 3.25). DL0 is a commercially available compound, and was used as purchased. The synthesis of 20 was attempted through several known methods, however, none were successful.38-40 Our lab has UV filtered yellow lighting and we found that 20 is only made under exposure to white light. Compound 20 cannot be used directly in the polymerization due to cyclization of the phenol-alkyne functionalities into a benzofuran (Figure 3.26),41 so it was necessary to protect the phenol group. From 20, three different protected products were made (DL1, DL2 and DL3) and tested in the polymerization.
Figure 3.25. The synthesis of four di(iodo)aromatic linkers used in this study. **DL0** is a commercially available compound. **DL1**, **DL2** and **DL3** were derived from 20 and each contains a different protecting group.

Figure 3.26. The palladium-catalyzed cyclization of \(o\)-hydroxy-alkynylbenzenes into benzofurans. Because of this cyclization, it is necessary to protect the hydroxyl group.\(^{46}\)

**Developing Polymerization Conditions.** To make acid cleavable polymers, it was necessary to find a polymerization method. There are few literature examples of polymers made from the palladium-catalyzed Hiyama coupling reaction,\(^{42,43}\) none containing electron- withdrawing groups conjugated with the reacting alkyne (i.e. carbonyl). This type of functionality is well understood, however for molecular compounds.\(^{44-46}\)
Preliminary polymerization resulted in an air-sensitive polymer. **DL0** and **CA1** were reacted under Hiyama conditions and a high molecular weight was detected by gel permeation chromatography (GPC). Upon precipitation, however, the light brown solid which was soluble in tetrahydrofuran (THF) quickly became black and insoluble when exposed to air. One possible explanation for the change in solubility of the polymer is ortho-palladation.\(^{47-51}\)

Ortho-Palladation is a known reaction where Pd(II) inserts itself into the ortho-position of an activated aromatic compound. The most common activating group is the amino-group,\(^{47,48}\) however the alkyne is also a known activating group.\(^{49-51}\) If, during precipitation, the catalyst were bound to the alkynes, upon exposure to oxygen the palladium catalyst would oxidize and be in close proximity to several possible ortho-palladation sites (Figure 3.27). Since only a small amount of crosslinking would result in insoluble polymer, it is conceivable that the palladium is the cause for the rapid change in solubility.

**Figure 3.27.** The ortho-palladation reaction. When the palladium is in solution, the catalyst is a Pd(0) complex, however, when the polymer is precipitated it is exposed to oxygen and in the condensed phase. Oxidation of the palladium, followed by two ortho-palladation reactions would result in polymer crosslinking.
To remove the palladium, we sequentially used three known methods for palladium removal.\textsuperscript{52,53} Upon reaction completion, the solution was heated with aqueous sodium bisulfate and thiourea, followed by a commercial palladium scavenger before precipitation. The precipitated solid should be completely free of palladium, and shows much better air stability, but still becomes insoluble in air. This crosslinking has prevented the testing of these systems as photoresists (the polymer crosslinks rapidly in thin films).

Monomers \textbf{DL1}, \textbf{DL2} and \textbf{DL3} were each also combined with \textbf{CA1} and polymerized. Only a relatively small molecular weight was attained (~1000 Da). Since the same molecular weight was achieved for all three reactions, we theorize macrocycles are forming.\textsuperscript{54} The iodo-groups in \textbf{DL1}, \textbf{DL2} and \textbf{DL3} are \textit{meta}-substituted, and so force the chain to curve. If the chain curves enough, the reactive end groups could meet each other and react forming macrocycles.

**NMR and GPC Analysis of Chain-Scission.** To better understand these polymers, the chain-scission was monitored through both GPC and NMR. The copolymer of \textbf{DL0} and \textbf{CA1} (described in section 3.4.5) dissolved in THF was analyzed using NMR and GPC followed by addition of trifluoromethanesulfonic acid. The acid was quenched, followed by reanalysis by NMR and GPC. The GPC results show the molecular weight shift from 10 KDa (Figure 3.28A) down to 0.5 KDa (Figure 3.28B). If the polymer cleaved as predicted (Figure 3.2), the tertiary esters would be converted into vinyl groups. The NMR data shows the development of a peak at ~5 ppm which likely indicates a vinyl proton supporting this scission (Figure 3.29).
Figure 3.22. GPC results of polymer chain-scission. A) GPC analysis of polymer before acid addition (~10 KDa). B) GPC analysis of polymer after acid addition (~0.5 KDa).

Figure 3.29. NMR results of polymer chain-scission. (A) Slight peak at 5 ppm shows little or no vinyl protons before acid addition. (B) After acid addition, a large peak develops, indicating the creation of vinyl protons.
3.5 Summary and Conclusions.

During the course of this work, a number of questions were investigated and addressed about acid cleavable chain-scission polymers:

**Can acid-cleavable polymers be made and how do they function as resists?**

Three generations of acid-cleavable chain-scission polymers have been designed and synthesized.

- **Generation I** polymers were made through the polyesterification reaction of a diol and a di(acid chloride). Generation I was found to have promising results with imaging down to ~30 nm, but had reproducibility issues likely due to the reactivity of the acid chloride.

- **Generation II** polymers were made through the polyether condensation reaction of acid- cleavable α-chloroesters and di(hydroxyl)aromatic linkers. Generation II was found to have very high resolution capabilities with patterning down to ~22 nm and modulation down to 14 nm, however, there were several causes of poor pattern quality. The pattern had serpentine deformation and bridging which we reason is a result of the low Tg and poor hydrophobicity caused by the ether linkages.

- **Generation III** polymers were made through the palladium-catalyzed polycoupling reaction of an acid-cleavable di(trimethylsilylalkyne) and a dihalobenzene. Although polymers were made, air stability was problematic and caused rapid crosslinking which we think is due to ortho-palladation in the condensed phase. Removal of the palladium does slow this crosslinking, however, polymers are still too unstable to test as thin films.
How do the mechanical and physical properties of the polymer affect the lithographic performance of these chain-scission resists?

The modeled polymer Tg for several chain-scission resist systems was compared. Polymer C was predicted to have a Tg of 50 °C while polymer F was predicted to have a Tg of 90 °C. Polymer F was found to have far better imaging than polymer C; we reason this is due to a control of acid diffusion associated with this change in Tg. When polymer C was first evaluated, the PEB (110 °C) was much higher than the Tg, resulting in rampant diffusion of the photoacid and complete scission of the exposed region.\textsuperscript{15-17} When the temperature was decreased (70 °C), diffusion was controlled and imaging was achieved. The image quality for polymer C, was not able to match the image quality of polymer F, which is likely due to the higher Tg of polymer F.

Can high Tg, hydrophilic resist polymers be made using the palladium catalyzed Hiyama coupling reaction?

Hiyama-coupled chain-scission polymers were made, but found to be air sensitive. An acid cleavable di(trimethylsilylalkyne) (CA1) was made and polymerized with diiodobenzene (DL0). The polymer made was found to crosslink in air, which is likely due to ortho-palladation. All attempts to completely remove palladium failed. The polymer was tested for acid sensitivity; GPC and NMR results indicated a significant loss in molecular weight upon exposure to acid. Three protected diiodophenols (DL1-DL3) were made and polymerized with CA1 and polymers were made, but only low molecular weights were achieved, likely due to macrocycle formation.
3.6 Experimental Methods.

General. All reactions were carried out under a nitrogen atmosphere. The reagents 5-hydroxyisophthalic acid, chloroacetic anhydride, acetic anhydride, and isophthaloyl chloride were purchased from Alfa Aesar. 3-Hexene-2,5-diol was purchased from TCI America and all other reagents were purchased from Sigma Aldrich. Trimethylsilylpropynoyl chloride was made by a previously reported method.37 Pyridine and triethylamine were dried by distillation over potassium hydroxide pellets and stored under nitrogen with 4Å-molecular sieves. All other reagents were used as received unless otherwise specified.

Instruments. Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker 400 spectrometer. All chemical shifts are reported as parts per million (ppm) relative to residual proton peaks of the deuterated solvent. Polymer molecular weights were determined using a Waters 1525 binary high pressure liquid chromatograph (HPLC) equipped with a Styrgel HR 4E THF gel permeation column and a Waters 2487 dual λ Absorbance Detector set at 280 nm. The column was calibrated using Fluka ReadyCal Set M(p) 250-70’000 polystyrene standards.
Synthetic Procedures.

\[
\begin{align*}
\text{HO-C-CH}_2\text{-CH}_2\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} & \quad \xrightarrow{\text{Cl}} \quad \text{HO-C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl} \\
\text{HO-C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl} & \quad \xrightarrow{\text{OH}} \quad \text{HO-C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CO}_2\text{H}
\end{align*}
\]

2,5-Dimethylhexane-2,5-diy l bis(2-chloroacetate) (CM1) (2). Compound 1 [2,5- dimethylhexane-2,5-diol] (1.46 g, 10 mmol), chloroacetic anhydride (17.10 g, 100 mmol), and hexane (200 mL) were combined in a flask equipped with a magnetic stir-bar and refluxed overnight. After refluxing, the solution was cooled to room temperature and slowly quenched with aqueous 5 % sodium carbonate solution. The organic phase was then washed with 5 % sodium carbonate followed by brine solution. The organic phase was dried over sodium sulfate and evaporated to yield a yellow, low melting solid. \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta\) 3.96 (4 H), 1.83 (4 H), 1.45 (12 H).

2,5-Dimethylhexane-2,5-diy l bis(2-hydroxyacetate) (CD2) (3). Triethylamine (TEA) (2.23 g, 22 mmol) was weighed into a flask and cooled to 0 °C. Formic acid (0.92 g, 20 mmol), was added drop-wise to the TEA while stirring. One equivalent of compound 2 (0.30 g, 1.0 mmol) was added to the solution and the mixture was stirred at room temperature for three days. The reaction mixture was eluted through a silica plug with a solution of 25 % ethyl acetate in hexanes. The eluent was then washed with 1 N hydrochloric acid followed by 5 % sodium carbonate. The solvent was evaporated and the crude product was dissolved in a 25 mL solution of 50/50 (v/v) acetone/saturated sodium bicarbonate. The solution was stirred for three days and then extracted.
with ethyl acetate. The ethyl acetate was evaporated and the product was recrystallized from boiling hexanes. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 4.00 (4 H), 3.41 (2 H), 1.84 (4 H), 1.36 (12 H).

5-Acetoxyisophthalic acid (5). Adapted from the literature procedure by Baek et al.$^{19}$ Compound 4 [5-hydroxyisophthalic acid] (9.106 g, 50 mmol) was combined with acetic anhydride (50 mL, 450 mmol) in a round-bottom flask equipped with a magnetic stir-bar and a reflux condenser. The solution was refluxed overnight. The reaction was cooled to room temperature and ice water was slowly added to the solution while stirring. The solution was stirred until a white precipitate formed. The precipitate was collected by filtration and dried by heating at 100 °C under reduced pressure yielding a white fluffy solid. mp > 200 °C $^1$H NMR (400 MHz DMSO) $\delta$ 13.30 (broad), 8.31 (1 H), 7.86 (2 H), 2.27 (3 H).

5-Acetoxyisophthaloyl chloride (AIC) (6). Adapted from the literature procedure by Baek et al.$^{19}$ Thionyl chloride (15 mL) was added to compound 5 (0.11 g, 0.5 mmol), followed by two drops of N,N-dimethylformamide (~ 0.01g, 0.02 mmol). The solution was refluxed overnight. The solvent was distilled off to give a crude oily mixture. The desired product was recrystallized
from hexane, filtered, and dried under vacuum. The product was distilled at 160 °C under vacuum (1 mmHg) and recrystallized from boiling hexane to produce yellow needles. mp 47-48 °C. $^1$H NMR (400 MHz DMSO) δ 8.30 (1 H), 7.85 (2 H), 2.26 (3 H).

**tert-Butyl 2-hydroxyacetate (8).** Adapted from the literature procedure by Li et al. $^5$ Triethylamine (2.23 g, 22 mmol) was placed in a flask and cooled to 0 °C. Formic acid (0.92 g, 20 mmol) was then added drop-wise to the triethylamine while stirring. One equivalent of compound 7 [tert-butyl chloroacetate] (0.30 g, 2 mmol) was added and the solution was stirred for three days at room temperature. The reaction was eluted through a silica plug with a solution of 25 % ethyl formate in pentane. The eluent is washed with 1 N hydrochloric acid followed by 5 % sodium carbonate. The solvent was evaporated and the crude product was dissolved in 50/50 (v/v) acetone/saturated sodium bicarbonate solution. The solution was stirred for three days and the desired product was extracted by continuous diethyl ether extraction. The ether was dried over sodium sulfate and evaporated to yield a clear oil. $^1$H NMR (400 MHz CDCl$_3$) δ 4.00 (2 H), 2.40 (1 H), 1.47 (9 H).

**Bis(2-tert-butoxy-2-oxoethyl)5-acetoxyisophthalate (Pentaester Model) (9).** 2,4,6- Trimethylpyridine (0.36 g, 3 mmol), 4-(N,N-dimethylamino)pyridine (0.01 g, 0.05 mmol), and tert-butyl 2-hydroxyacetate (0.396 g, 3 mmol)
were added to a solution of compound 6 (0.26 g, 1 mmol) in toluene (5 mL). The solution was stirred for one hour. The solution was then washed with 1 N hydrochloric acid, 5 % sodium carbonate, and lastly with brine. The organic phase was dried over sodium sulfate and evaporated under reduced pressure to yield a white solid. \(^1\)H NMR (400 MHz 50/50 (v/v) d4-Methanol / d6-DMSO) δ 8.30 (1 H), 7.85 (2 H), 4.73 (4 H), 2.26 (3 H), 1.39 (18 H).

![Chemical structure](image)

2,2'-(1,4-Phenylene)bis(propane-2,2-diyl) bis(2-chloroacetate) (CM2) (11).

Compound 10 [1,4-bis(2-hydroxyisopropyl)benzene] (5.0 g, 25.7 mmol), chloroacetic acid (14.6 g, 155 mmol), and 4-(N,N-dimethylamino)pyridine (18.9 g, 155 mmol) were combined in a 1 L flask equipped with a stir bar and dissolved in 0.3 L of toluene (anhydrous). In a separate 200 mL flask, N,N-dicyclohexylcarbodiimide (DCC) (31.9 g, 155 mmol) was dissolved in anhydrous toluene (100 mL). The solution containing the DCC was slowly added to the reaction flask over the course of 10 minutes and the reaction was allowed to stir for 4 hours at ambient temperature. During the 4 hours a white precipitate formed. The solution was then filtered through a short silica plug and the solvent was removed under vacuum. The crude product was then purified by chromatography using silica gel as the stationary phase and hexane and methylene chloride as the mobile phase, producing a viscous oil.
$^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.33 (4 H), 4.01 (4 H), 1.80 (12 H).

[2,2'-(5-Hydroxy-1,3-phenylene) dipropan-2-ol (13). Adapted from the literature procedure by Shibuya et al.$^{56}$ Compound 12 (diethyl 5-hydroxyisophthalate) (4.7 g, 20 mmol) dissolved in anhydrous diethyl ether (200 mL) in an oven-dried 500 mL flask equipped with a reflux condenser and stir-bar and anhydrous toluene (200 mL) was added. Upon cooling in an ice bath, a bubbler was attached to the system and N$_2$ was bubbled through the reaction mixture for 10 minutes. Methylmagnesium bromide (3 N, 70 mL) was added drop-wise, while stirring. The reaction mixture was then removed from the ice bath and set to reflux overnight. Upon completion, the solution was cooled with an ice bath and quenched slowly with 1 N hydrochloric acid. The aqueous phase was then extracted three times with ethyl acetate, the organic phases were combined and solvent was removed under reduced pressure. The crude product was then dissolved in deionized water and washed three times with methylene chloride. The methylene chloride was discarded, and the aqueous phase was then extracted three times with ethyl acetate. The solvent was removed and the compound was crystallized in dibromomethane to yield colorless needles (3.5 g, 83 % yield). $^1$H NMR (400 MHz CD$_3$NO$_2$) $\delta$ 8.56 (1 H), 7.08 (1 H), 6.79 (2 H), 3.54 (2 H), 1.44 (12 H).
[2,2’-(5-Acetoxy-1,3-phenylene) dipropan-2-ol (14).] Compound 13 (2.0 g, 9.5 mmol) was dissolved in anhydrous diethyl ether (80 mL) and anhydrous tetrahydrofuran (20 mL) in a 250 mL round-bottom flask equipped with a stir bar. The solution was cooled using an ice bath, then triethylamine (1.9 g, 19 mmol) followed by acetic anhydride (1.9 g, 19 mmol) were added drop-wise to the flask. The solution was stirred overnight then washed three times with saturated aqueous carbonate, followed by one wash with 1 N hydrochloric acid. The organic phase was then removed under reduced pressure and the compound was crystallized in methylene chloride and hexane to produce colorless crystals. $^1$H NMR (400 MHz CD$_3$NO$_2$) $\delta$ 7.52 (1 H), 7.07 (1 H), 2.24 (3 H), 1.51 (12 H).

2,2’-(5-Acetoxy-1,3-phenylene)bis(propane-2,2-diyl)bis(2-chloroacetate) (CM3) (15). Compound 14 (7.1 g, 28 mmol), chloroacetic acid (15.9 g, 168 mmol), and 4-(N,N-dimethylamino)- pyridine (20.5 g, 168 mmol) were combined in a 1 L flask equipped with a stir bar and dissolved in 0.32 L of toluene (anhydrous). In a separate 200 mL flask, N,N-dicyclohexylcarbodiimide (DCC) (34.7 g, 168 mmol) was dissolved in anhydrous toluene (100 mL). The solution containing the DCC was slowly added to the reaction flask over the course of 10 minutes and the reaction was allowed to stir for 4 hours are ambient temperature. During the 4 hours a white precipitate formed. The solution was then filtered through a short silica plug and the solvent was removed under vacuum. The crude product was then purified by chromatography using silica gel as the stationary phase and
hexane and methylene chloride as the mobile phase, producing a viscous oil.

$^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.27 (1 H), 7.01 (2 H), 4.00 (4 H), 2.28 (3 H), 1.79 (12 H).

![Chemical Structures](image)

**tert-Butyl 2-(3,5-dihydroxyphenoxy)acetate (TBE) (17).** *tert*-Butyl chloroacetate (9.5 g, 52 mmol) and potassium carbonate (32.3 g, 0.23 mol) were combined with anhydrous $N,N$-dimethylformamide (200 mL) in a 250 mL round-bottom flask equipped with a stir bar. Compound **16** (phloroglucinol) (20.0 g, 0.16 mol) and potassium iodide (0.86 g, 5 mmol) were then added and the solution was stirred at ambient temperature for 12 hours. Upon completion, ethyl acetate (200 mL) was added and the reaction mixture was filtered through a glass fritted funnel. The liquor was then concentrated and poured into 1 N hydrochloric acid at 0 °C and extracted twice with methylene chloride. The organic phases were then combined, washed with brine and condensed under reduced pressure. The crude product was then chromatographed using methylene chloride and ethyl acetate to yield a clear, viscous oil. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 5.96 (3 H), 4.41 (2 H), 1.45 (9 H).
2,5-Dimethylhexane-2,5-diyl di(trimethylsilylpropyoyate) (CA1) (18).

Compound 1 [2,5-dimethylhexane-2,5-diol] (1.46 g, 10 mmol) was placed in an oven-dried round-bottom flask equipped with a stir-bar and placed under nitrogen and equipped with a mineral oil bubbler. Anhydrous tetrahydrofuran (30 mL) was then added and the flask was placed in a dry ice/acetone bath and stirred for 10 minutes. Methyllithium (21 mmol, 7 mL, 3N in tetrahydrofuran) was then added drop-wise and the solution was stirred at room temperature for 1 hour. The flask was again placed in a dry ice/acetone bath and stirred for 10 minutes before trimethylsilylpropynoyl chloride (3.31 g, 21 mmol) dissolved in THF (10 mL) was added drop-wise. After addition, the reaction was brought to room temperature and stirred overnight. The reaction flask was then quenched with water and extracted with hexane and run through a silica plug, eluting with 90 % hexane in methylene chloride. The organic phase was condensed under reduced pressure and crystallized from methanol. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 1.65 (12 H), 1.57 (4 H), 0.22 (18 H).
2,4-Diiodophenol (20). Adapted from the literature procedure by Edgar et al.\textsuperscript{40} Compound 19 [4-iodophenol] (2.20 g, 10 mmol) was placed in a round-bottom flask equipped with a magnetic stir-bar and dissolved in methanol (10 mL). Potassium iodide (1.83 g, 11 mmol) dissolved in water was added to the flask while stirring. The flask was illuminated with a standard tungsten-filament lamp and a sodium hypochlorite solution (5.25 %, 9.9 mL) was added drop-wise. The reaction was then stirred for 30 minutes, followed by extraction with diethyl ether. The ether was removed under reduced pressure and the crude product was purified by chromatography using silica gel as the stationary phase and hexane and methylene chloride as the mobile phase, producing a white solid. \textsuperscript{1}H NMR (400 MHz CDCl\textsubscript{3}) \(\delta\) 7.91 (1 H), 7.47 (1 H), 6.75 (1 H), 5.28 (1 H).

**General Procedure for 21 through 23 [Protected 2,4-diiodophenols (DL1-DL3)].** Compounds 21 through 23 were made by the same general method. Compound 20 (1 molar equivalent) was combined with sodium hydroxide (1.1 molar equivalents) in methanol (10 mL / 1 molar equivalent) in
a round-bottom flask equipped with a magnetic stir-bar. The solution was warmed and stirred until solids were dissolved (~10 minutes). The solvent was removed under reduced pressure and the solids were azeotropically dried under reduced pressure with toluene. The white solids were then dissolved in anhydrous tetrahydrofuran (10 mL / 1 molar equivalent) and the appropriate protecting group starting material was added. The flask was equipped with a reflux condenser and refluxed for 30 minutes, followed by solvent removal under reduced pressure. The crude product was dissolved in methylene chloride, washed with 1 N sodium hydroxide solution, dried over sodium sulfate and the solvent was removed under reduced pressure.

**Acetate-protected 2,4-diiodophenol (DL1) (21).** $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.12 (1 H), 7.62 (1 H), 6.83 (1 H), 2.83 (3 H).

**(p-Methyl-benzoate)-protected 2,4-diiodophenol (DL2) (22).** $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.16 (1 H), 8.10 (2 H), 7.67 (1 H), 5.32 (2 H), 6.99 (1 H), 2.44 (3 H).

**(Methoxymethyl ether)-protected 2,4-diiodophenol (DL3) (23).** $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.03 (1 H), 7.51 (1 H), 6.81 (1 H), 5.19 (2 H), 3.47 (3 H).

**Generation I Polymer Synthesis.** One equivalent of acyl chloride was placed in a dry Erlenmeyer flask equipped with a magnetic stir-bar and cooled in an ice bath. A 4-(N,N-dimethylamino)pyridine solution (0.6 N in pyridine) was added to the diol (10 % w/w diol) and dried over 4Å molecular sieves. One equivalent of diol solution is added quickly to the acyl
chloride while stirring. The solution is allowed to stir for ten minutes, then the reaction is quenched with excess methanol in acetone. The solution is slowly dripped into a large excess of 1N HCl. The precipitate is collected, redissolved in acetone and precipitated in 1N HCl. The polymer is collected and dissolved in dimethylsulfoxide (10 mL / g of polymer). A solution of isopropyl alcohol (50 mL) and 0.44 mL of 28 % w/w aqueous ammonia is added slowly to the polymer solution and stirred for 1 hour. After 1 hour the solution is added dropwise to a large excess of 1N HCl. The precipitate is collected, dissolved in acetone and reprecipitated in 1N HCl. The precipitate is then filtered and dried under vacuum.

**Generation II Polymer Synthesis.** Compounds CM1 (2.39 g, 8 mmol) or a combination of CM2 (0.56 g, 1.6 mmol) and CM3 (2.59 g, 6.4 mmol) were mixed with TBE (0.38 g, 1.6 mmol) and BPA (1.46 g, 6.4 mmol) in a round bottom flask equipped with a stir-bar and bubbler. Anhydrous N,N-dimethylformamide (20 mL) and sodium carbonate (17.0 g, 160 mmol) were then added and nitrogen was bubbled through the solution for 10 minutes. The reaction mixture was then heated to 60 °C and stirred for 48 hours upon which the solution was precipitated into 1 N hydrochloric acid. The precipitate was then collected and dissolved in dimethylsulfoxide (20 mL). A solution of isopropyl alcohol (50 mL) and 0.44 mL of 28 % w/w aqueous ammonia was added slowly to the polymer solution and stirred for 1 hour. After 1 hour the solution was added drop wise to a large excess of 1 N HCl. The precipitate was then filtered and dried under vacuum.


**Generation III Polymer Synthesis.** Adapted from the modified literature procedures.\textsuperscript{44-46} Two round-bottom flasks were oven-dried. The primary reaction flask (flask A) was fitted with a reflux condenser and magnetic stir-bar and placed under argon. DL1 (1.65 g, 5 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.58 g, 0.5 mmol) were placed in flask A and silver nitrate (0.85 g, 5 mmol) and CA1 (1.97 g, 5 mmol) were placed in flask B. To both flasks, anhydrous tetrahydrofuran (20 mL) was added and argon gas was bubbled through for 10 minutes. Flask B was cooled to 0 °C and tetrabutylammonium fluoride (10 mmol, 10 mL, 1 N in tetrahydrofuran) was added drop-wise followed by stirring for 30 minutes. The contents of flask B were then added by cannula to flask A and flask A was refluxed overnight. A solution of sodium bisulfite (12.0 g, 100 mmol) and thiourea (1.5 g, 20 mmol) dissolved in water (20 mL) was degassed with argon, added to the reaction flask and the contents were refluxed an additional 30 minutes. The mixture was then extracted with three times with ethyl acetate, reduced under vacuum and precipitated in 50% methanol in water, followed by reprecipitation with hexane from methylene chloride. The resulting solid was then dried under reduced pressure.
Table 3.4. Processing conditions for EUV exposure.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Wt % PAG</th>
<th>Wt% TBAH</th>
<th>PAB (°C/s)</th>
<th>PEB (°C/s)</th>
<th>Developer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>7.5</td>
<td>0.5</td>
<td>130/60</td>
<td>110/90</td>
<td>0.04 N TMAH</td>
</tr>
<tr>
<td>C</td>
<td>7.5</td>
<td>0.5</td>
<td>130/60</td>
<td>110/90</td>
<td>0.03 N TMAH</td>
</tr>
<tr>
<td>D</td>
<td>7.5</td>
<td>0.5</td>
<td>130/60</td>
<td>110/90</td>
<td>0.03 N TMAH</td>
</tr>
<tr>
<td>E</td>
<td>7.5</td>
<td>0.5</td>
<td>130/60</td>
<td>110/90</td>
<td>0.13 N TMAH</td>
</tr>
<tr>
<td>F</td>
<td>7.5</td>
<td>0.5</td>
<td>130/60</td>
<td>110/90</td>
<td>0.03 N TMAH</td>
</tr>
<tr>
<td>G</td>
<td>15</td>
<td>1.5</td>
<td>110/60</td>
<td>None</td>
<td>20% (0.26 N TMAH)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80% Isopropanol</td>
</tr>
<tr>
<td>H</td>
<td>15</td>
<td>1.5</td>
<td>110/60</td>
<td>None</td>
<td>20% (0.26 N TMAH)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80% Isopropanol</td>
</tr>
</tbody>
</table>

General Resist Formulations and Imaging. Resists were prepared in ethyl lactate (EL)/propylene glycol methyl ether acetate (PGMEA) (50/50 wt %). The solid components were formulated with weight percents (wt %) of iodonium nonaflate photoacid generator (PAG), tetrabutyl ammonium hydroxide (TBAH) as shown in Table 3.4, with the remaining mass being polymer. The resist solutions were filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane filter. The developer concentrations were adjusted to produce an unexposed film thickness loss (UFTL) of 5 to 10%. Both evaluations of resist B are shown in Table 3.4. Polymer G was tested both with no PEB and a PEB of 110 °C for 60 seconds with no change to imaging.
3.7 References.


21. Monoreacting functional groups will inhibit high molecular weight growth by forming the chain ends

22. Ramanathan, M., and Darling, S. B., Progress in Polymer Science (2011) 36, 793


44. Lecercle, D., *et al.*, *Synthetic Communications* (2007) **37** (8), 1301


Chapter IV

Ligand Design for Hafnium Nanoparticle Resists

4.0 Overview.

Chapter IV focuses on the study and development of ligands for hafnium-oxide nanoparticle based photoresists. Christopher Ober and Emmanuel Giannelis at Cornell University, have developed a hafnium-oxide nanoparticle photoresist system based on the free-radical crosslinking of nanoparticle ligands. This chapter focuses on a collaborative work we performed to understand and improve this system. Here we describe a ligand binding study which was performed to measure the relative binding energies for a series of different functional groups, followed by the development of two ligand sets containing a strong-binding functionality, one set capable of free-radical crosslinking and one set capable of increasing aqueous developer solubility.

4.1 Introduction.

As resolutions improve, film thicknesses must like-wise decrease to prevent pattern collapse. As film thicknesses decrease, however, etch processes struggle to meet the etch requirements for current and future fabrication nodes. Cornell has recently developed a novel organic-inorganic resist system composed of a hafnium or zirconium oxide nanoparticle core and a shell composed of organic methacrylate ligands. These resists (Figure 4.1) are
designed to crosslink the nanoparticle films by a basic free-radical polymerization mechanism and combine excellent etch rates with high sensitivity in EUV. Although these systems show great promise, one concern is agglomeration. Nanoparticles are small particulates with high surface energies due to large surface-to-volume ratios.\textsuperscript{7} If the methacrylate ligands are weakly bound, the nanoparticles may agglomerate, potentially limiting the shelf-life and lithographic performance, resulting in defects and poor LER.

The goal of this study was to design a set of new ligands that would have strong-binding to the nanoparticle while enabling optimization of the Cornell nanoparticle resists. To prevent agglomeration, our ultimate goal was to create ligands with strong binding functionalities. First we performed a ligand binding study for a series of functional groups to determine the functionality with the strongest binding energy. We then designed a series of ligands based on that strong-binding functionality that are capable of crosslinking the nanoparticles and enabling the nanoparticles to use aqueous developer.
Figure 4.1. The Cornell nanoparticle resist consists of a nanoparticle core and a methacrylate shell (left). This system of resists has high resolution imaging at extremely fast photospeeds.  

4.2 Ligand Binding Studies.

In order to optimize the nanoparticle resist systems to prevent agglomeration, it was important to have a method to evaluate the strength of the interaction between ligand and nanoparticle. Typically for a ligand binding study, the absolute ligand binding energy could be determined by measuring the concentration of “bound” and “unbound” ligands at equilibrium, and relating them through the equilibrium constant. For the case of the hafnium oxide nanoparticles with carboxylate ligands, however, the “unbound” case results in highly reactive nanoparticles which can agglomerate, skewing the results. The goal of this study is to optimize the ligand binding
strength, which can be accomplished through comparison of binding energies relative to a control ligand.

In order to measure these relative binding energies, nanoparticles with a single control ligand could be combined with a second ligand in solution and allowed to reach exchange equilibrium (Figure 4.2). The relative concentration of each ligand, both in solution and bound to the nanoparticle, could then be measured using NMR, and the relative binding energy would be determined through the equilibrium constant as described by equations 4.1 and 4.2.

![Figure 4.2](image)

**Figure 4.2.** A nanoparticle with L₁-bound ligand is combined with a second ligand L₂ in solution. After equilibrium has been reached, the concentrations of L₁ and L₂, both free in solution and bound to the nanoparticle are measured.

\[
K_{eq} = \frac{[L_1^{Sol.}][L_2^{Bound}]}{[L_1^{Bound}][L_2^{Sol.}]}
\]

**Equation 4.1.** The equilibrium constant (K<sub>eq</sub>) is equal to the concentration of L₁ in solution (L₁<sup>Sol.</sup>) over the concentration of L₁ bound to the nanoparticle (L₁<sup>Bound</sup>) multiplied by the concentration of L₂ bound to the nanoparticle (L₂<sup>Bound</sup>) over the concentration of L₂ in solution (L₂<sup>Sol.</sup>).
\[ \Delta G_{\text{Rel.}}^0 = -RT \ln(K_{eq.}) \]

**Equation 4.2.** Gibbs Free Energy. The relative change in the gibbs free energy (\( \Delta G_{\text{Rel.}}^0 \)) is equal to negative the temperature (T) multiplied by the universal gas constant (R) multiplied by the natural log of the equilibrium constant (\( K_{eq.} \)).

Nuclear Magnetic Resonance (NMR) uses a radio signal to perturb the nuclear spin of an atomic nucleus precessing in a strong magnetic field. \(^8\)\(^9\) After a given amount of time (relaxation time), the perturbed nucleus will return to a thermal equilibrium state. During this perturbation, data acquisition occurs by measurement of the radio frequency that is emitted by the relaxing nucleus. Initial attempts to measure the equilibrium concentrations of ligands bound to the nanoparticles and free in solution were unsuccessful due to the rapid ligand-exchange rates. If the ligand exchange is faster than the relaxation of the perturbed nucleus, the perceived signal will be an average of the individual signals for the bound and free ligands (Figure 4.3).
Figure 4.3. (A) A representative NMR spectra of a ligand bound to the nanoparticle and free in solution, indicating that the rate of exchange is slow enough to resolve. (B) A representative NMR spectra of an averaged peak due to the fast exchange of ligands.

Dynamic NMR is a method commonly used to resolve rapidly exchanging species by cooling the sample during acquisition.\textsuperscript{10,11} We performed preliminary dynamic measurements on the nanoparticle ligand exchange at -60 °C. Acetate nanoparticles were mixed with trifluoroacetic or formic acid. The trifluoroacetate/acetate system did not result in separation of the peaks, suggesting that the ligand exchange was too fast to be measurable by even dynamic NMR. The formate/acetate system, however, did show peak separation between the bound formate and formic acid in solution. But, upon removal of the NMR tube from the spectrometer, we found that precipitation had occurred, changing the relative concentration of the detected ligands in solution. Several other solvent systems were tried, however none resulted in a stable solution with a freezing point below -60 °C. Several alternate NMR techniques were attempted to directly measure ligand concentrations bound and in solution, but none were found to work for this system.
Nanoparticle Precipitation. We found the best way to measure the relative ligand binding energies was to use a precipitation method to trap the equilibrium concentration of ligand bound to the nanoparticles. Here, a sample of nanoparticles was combined with a large excess of two ligands of known concentration. The solution was allowed to equilibrate and then dripped into a precipitation solution, resulting in precipitation of the nanoparticles. It was important to find precipitation solutions which allowed precipitation of the nanoparticles, yet miscible with both free ligands.

After precipitation, and two subsequent washes, the precipitated nanoparticles were dried under vacuum and the relative concentrations of each ligand were measured by NMR. The procedure was repeated using several different ligand solution concentrations. Since the solution ligand concentrations are known for each point, the data set was able to be fit with equation 4.1. The fit $K_{eq}$ was then used to calculate the relative binding energy ($\Delta G^{\circ}_{rel}$) using equation 4.2 (Figures 4.4 and 4.5).

Ligand Binding Results. A total of fifteen potential ligands were investigated in this study. The ligands that did not produce measureable results fell into one of three categories:

- The organophosphonate ligands tested formed insoluble precipitates and NMR could not be performed.
- The amide ligands formed completely miscible solutions and could not be separated by precipitation.
• Other ligands did not bind well enough to the nanoparticles to be detected by NMR.

The remaining ligands successfully bound to the nanoparticles and thermodynamic data was collected (Figure 4.4). All the binding energies were measured relative to acetic acid. Thioacetic acid was found to have the weakest bond, with a binding energy greater than that of acetic acid. Malonic acid made insoluble precipitates in concentrations greater than 1% which may be due to crosslinking of the nanoparticles. Methanesulfonic acid was found to have the strongest binding energy: 2.0 kcal/mol more stable than acetic acid. Due to the apparent strength of the sulfonate nanoparticle interaction, further studies were performed using sulfonates as the strong binding functionality
**Figure 4.4.** Equilibrium concentrations of bound ligand were measured as a function of ligand solution concentration for three ligand types. Experimental data was then fit with equation 1, and the equilibrium constants were obtained.

**Figure 4.5.** The relative binding energies were calculated from equation 2 for each of these five ligands. Methanesulfonic acid was found to have the strongest binding, almost 2 kcal stronger than acetate.
4.3 Strong Binding Free-Radical Monomer Ligands.

The ultimate goal of this work is to develop a method to optimize nanoparticle resists. The original methacrylate ligand can be separated into two functionalities: an attachment group (carboxylate) and a cross-linkable group (activated olefin). Sulfonate ligands were found to have a much stronger bond to the hafnium oxide nanoparticles than carboxylates, therefore, replacing the carboxylate group with a strong-binding sulfonate should prevent agglomeration. However, an optimized photoresist is a fine balance of many different parameters. By developing a series of sulfonate ligands with cross-linkable groups of varied reactivity, the lithographic performance can be further optimized through formulation (Figure 6).

![Diagram](image.png)

**Figure 4.6.** Strategic design of cross-linkable ligands. (A) The ligands bound to the nanoparticle can be subdivided into functionalities: an attachment group and a cross-linkable group. (B) By changing the attachment group from a carboxylate to a sulfonate and then varying the reactivity of the cross-linkable group, a series of strong-binding ligands can be designed to optimize lithographic properties.
In order to have control over the reactivity of the nanoparticle crosslinking reaction, a ligand set was designed based from common free-radical monomer types of known reactivity. The relative reactivity towards free-radical polymerization is well known for common free-radical monomer types. Styrenes, acrylates and aliphatic olefins are known to have much different reactivity toward free-radical polymerization. By using these functionalities as the cross-linkable groups, and designing a series of ligands around them, the reactivity of the nanoparticles to cross-linking can be optimized through formulation. The three sulfonate ligands (Figure 4.7) were designed with one of each of these cross-linkable groups and were either purchased or synthesized.

**Figure 4.7.** Three ligands were designed with strong binding sulfonate moieties, and also one of three cross-linkable groups of varied reactivity. Formulation of nanoparticle resists with these ligands will allow optimization of cross-linking chemistry.
4.4 Ligands for Aqueous Develop Nanoparticles.

Aqueous tetramethylammonium hydroxide (TMAH) is the most commonly used resist developer in semiconductor fabrication. Although there is a recent movement in the research community toward organic developers, flammability still remains a concern and the industry is hesitant to change. The Cornell nanoparticle resists currently use organic developers. To make this platform more flexible, we have developed a new set of ligands designed to be formulated with the cross-linkable ligands, and to give the nanoparticles solubility in aqueous developer (Figure 4.8).

![Figure 4.8](image)

Figure 4.8. Strategic design of ligands for aqueous solubility. (A) The ligands bound to the nanoparticle can be subdivided into functionalities: an attachment group and a solubility group. (B) A bidentate ligand (a ligand that can bind in two spots) could cause cross-linking between the nanoparticles. A monodentate ligand with aqueous solubility is ideal.

Most polar groups have been known to provide aqueous solubility to polymers, however many of these groups are also good ligands (i.e. carboxylic acids). If a single ligand were to ligate two nanoparticles, uncontrolled cross-linking would occur. Two commonly used solubility groups
which are also poor ligands are phenols and tertiary amines. Both of these groups should not cross-link the nanoparticles, however, they can both switch from ionic to non-ionic at relatively mild pH, increasing the nanoparticle aqueous solubility. Two sulfonate ligands, each with a different solubilizing group, were made and tested. Ligand \textbf{L4}, was found to have poor solubility when combined with the nanoparticles and so could not be cast. This ligand was then reengineered to have greater solubility by decreasing rigidity and symmetry, resulting in ligand \textbf{5} (Figure 4.9). Ligands \textbf{L5} and \textbf{L6} were both found to have good solubility in casting solvents, and so were spin coated and dissolution rates were tested. In both cases, dissolution rates were found to be greater than 100 nm/sec. Ultimately, we think these ligands can be combined with other ligands on the nanoparticles to produce resists with good lithographic properties using aqueous developer.
Figure 4.9. The synthesis of three ligands capable of making nanoparticle resists that use aqueous developer. Originally only one phenol ligand was planned, but due to solubility of the nanoparticles, a second ligand with higher solubility was made.

4.5 Lithographic Evaluations and Rethinking of Mechanism.

The sulfonate ligands made in this study were found to deactivate the nanoparticle imaging capabilities. Nanoparticles containing ligands 1 through 3 were made and tested by Cornell. Interestingly, when tested for imaging, no photosensitivity was found. This has led Cornell to investigate the mechanism of this photoreaction, and they have proposed a new mechanism.
Cornell has proposed a new mechanism for the nanoparticle photoreaction, involving the ligand exchange between generated photoacids and nanoparticle ligands.\textsuperscript{13} Cornell has studied the photosensitivity of nanoparticles with acrylates and isobutyrate, and has found very similar sensitivities. Since isobutyrate cannot crosslink, Cornell has concluded the mechanism for photoreaction is not crosslinking. Through spectroscopic and mass loss studies, Cornell has proposed a new mechanism which involves the generation and ligand exchange of sulfonates. The crosslinking initiator used in these studies was a commercial, non-ionic photoacid generator which generates trifluorosulfonic acid (Figure 4.10).\textsuperscript{14,15} Cornell has proposed the sulfonic acid created exchanges with the nanoparticle ligands, ultimately changing their solubility.

![Sulfonic Acid Reaction](image)

**Figure 4.10.** Generation of a sulfonic acid upon exposure. The exchange of that sulfonic acid with a carboxylate ligand results in a change in solubility.

### 4.6 Summary and Conclusions.

The relative ligand binding energies for a series of ligands has been investigated using a precipitation method followed by NMR. Malonic acid was
found to form insoluble precipitates in concentrations above 1%, which may be due to crosslinking of the nanoparticles. Thioacetic acid was found to have a binding strength weaker than acetic acid and methanesulfonic acid was found to have a binding energy 2.0 kcal/mol stronger than acetic acid. It was also found that many ligands either formed completely insoluble precipitates, formed solutions that did not precipitate, or did not form any observable bond to the nanoparticles.

To provide a system for lithographic optimization of the nanoparticle resist systems, a series of strong binding sulfonate ligands was designed that are capable of free radical polymerization. Three different free radical monomer types with different polymerization reactivities were investigated: styrene, methacrylate, aliphatic olefin. For each type, a sulfonate functionality was incorporated as the binding functionality. These ligands were made and are currently awaiting lithographic evaluation.

A second series of strong binding sulfonate ligands was designed to enable the nanoparticle resists to be developed using aqueous developer. Two solubilizing groups were investigated: phenols and amines. Three ligands were made containing sulfonates with either phenol or amine functionality. These ligands were bound to nanoparticles and tested for aqueous development; one was found to be too insoluble for any casting solvent tested, the other two were found to have dissolution rates greater than 100 nm/sec.
4.6 Experimental Methods.

Materials. The nanoparticles used in this study were hafnium oxide core nanoparticles with acetic acid ligands that were provided by Cornell. Unless otherwise stated, all ligands, solvents and starting materials were purchased from Sigma Aldrich. Formic acid, and acetic acid were purchased from Alfa Aesar. Methylene chloride and hexanes were purchased from Pharmco- Aaper. TMAH developer used was Microposit MF CD26.

Instruments. NMR experiments were performed on a 400 MHz Bruker FT-NMR with a standard broadband probe and liquid nitrogen cooling with D$_2$O or CD$_3$OD as the NMR solvent. Film thickness measurements were performed on a Dektak Profilometer.

General Procedure for the Ligand Binding Study. Ligand exchange was performed by combining the nanoparticles (20 mg) with a large excess of two ligands (10 total mmol) and sonicating for 10 minutes to promote exchange. By controlling the relative ligand concentrations of the two exchange ligands, the solution ligand concentration was known. The sonicated solution was then dripped into a hexane and methylene chloride mixture, resulting in precipitation of the nanoparticles but dissolution of the excess ligands. The solution was centrifuged, the supernatant was removed and the precipitate was washed twice with the hexane and methylene chloride mixture. The precipitate was then dried under reduced pressure.
Dissolution Rate Measurements. For each sample, 20 mmols of ligand was dissolved in 4 mL of 50 % methanol in water. 100 mg of nanoparticles with acetic acid ligands were dissolved in 2 mL of 50 % methanol in water and then added to the ligand solution. This mixture was sonicated for 10 minutes and then centrifuged. The precipitate was then washed twice with 50 % methanol in water and dried under reduced pressure.

Casting solutions were made by dissolving the nanoparticles (5% solids) in the appropriate casting solvent. The solutions were then filtered using a 0.2 µm pore PTFE syringe filter and spin coated to get a 100–nm thick film. Film thickness was measured by scratching the film and performing profilometry. Each wafer was then diced and placed into developer. After the allotted time, the wafer was then removed and washed with DI water, and dried using compressed air. For each case, complete film loss occurred after 1 second.

Synthetic Procedures.

\[
\begin{array}{ccc}
\text{Na}_2\text{SO}_3 + \text{OH}^- & \rightarrow & \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \\
\text{25} & \rightarrow & \text{26}
\end{array}
\]

Sodium 2-(methacryloyloxy)ethanesulfonate (26). Compound 25 [sodium 2-hydroxyethanesulfonate] (7.4 g, 50 mmol) was dissolved in trifluoroacetic acid (100 mL) in a 250 mL round-bottom flask equipped with a magnetic stir-bar. While cooling with an ice bath, methacryloyl chloride (26.1 g, 250 mmol) was added drop-wise. The solution was placed under nitrogen and allowed to stir overnight at room temperature. The reaction solution was then precipitated
into 20% methylene chloride in hexane by volume and a white solid was collected by filtration (8.2 g, 76 %). $^1$H NMR (400 MHz, D$_2$O) δ 1.89 (3 H), 3.28 (2 H), 4.49 (2 H), 5.69(1 H), 6.16 (1 H).

![Chemical structure](image1)

**Sodium prop-2-ene-1-sulfonate (28).** Adapted from the literature procedure by Jiang et al.$^{16}$ Compound 27 [allyl bromide] (17.3 mL, 200 mmol) and sodium bisulfite (18.9 g, 150 mmol) were dissolved in ethanol (150 mL) and water (50 mL) in a 250 mL round-bottom flask equipped with a magnetic stir-bar and a reflux condenser. The solution was refluxed overnight, then the solvent was removed under reduced pressure. The solid was then crystalized in acetone and wet ethanol to yield a crystalline solid (12.6 g, 58). $^1$H NMR (400 MHz, D$_2$O) δ 3.61 (2 H), 5.32 (1 H), 5.35 (1 H), 5.87 (1 H).

![Chemical structure](image2)

**Potassium 4-hydroxybenzenesulfonate (30).** Adapted from the literature procedure by Davies et al.$^{17}$ Compound 29 [$p$-fluorobenzenesulfonyl fluoride] (3.8 g, 20 mmol) was dissolved in isopropyl alcohol (20 mL) and water (60 mL) in a 100 mL round-bottom flask equipped with a magnetic stir-bar and a reflux
condenser. Potassium hydroxide (22 g, 400 mmol) was slowly added while stirring until completely dissolved. After refluxing overnight, the pH was brought to neutral using 1 N hydrochloric acid, the solvent was then removed under reduced pressure. The solid was then recrystallized in methanol and water to yield a white, crystalline solid (3.8 g, 89%). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 6.91 (2 H), 7.65 (2 H).

\[
\text{31} \xrightarrow{\text{OH}} \text{32} \xrightarrow{\text{Br}} \text{33}
\]

$m$-Hydroxybenzyl bromide (32). Adapted from the literature procedure by Scaramuzzino et al.$^{18}$ Compound 31 [m-hydroxybenzyl alcohol] (6.2 g, 50 mmol) was dissolved in a mixture of 33 % w/w hydrogen bromide in acetic acid (25 mL) and 48 % w/w hydrobromic acid (25 mL) in a 100 mL round-bottom flask equipped with a stir-bar. The flask was placed under nitrogen and stirred overnight. The solution was quenched with methylene chloride and water in a separatory funnel. The organic phase was then again washed with water and condensed under reduced pressure. The crude product was placed on a silica gel column and flashed with methylene chloride. The organic phase was then condensed under reduced pressure and recrystallized from methylene chloride and hexane to produce a crystalline solid (3.5 g, 37 % yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.42 (2 H), 4.76 (1 H), 6.77 (1 H), 6.86 (1 H), 6.94 (1 H), 7.19 (1 H).
**Sodium (3-hydroxyphenyl)methanesulfonate (33).** Compound 32 [m-hydroxybenzyl bromide] (3.5 g, 18.7 mmol) and ethanol (63 mL) was placed in a 100 mL round-bottom flask attached with a reflux-condenser and stir-bar. Sodium bisulfite (2.3 g, 18.7 mmol) dissolved in water (21 mL) was added to the reaction. The reaction mixture was refluxed overnight, then dried under reduced pressure and recrystallized from ethanol to yield a white crystalline solid (3.3 g, 84% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 4.23 (2 H), 7.02 (1 H), 7.04 (1 H), 7.11 (1 H), 7.42 (1 H).

![Chemical Structure](image)

**Sodium 2-(pyrrolidin-1-yl)ethanesulfonate (35).** Adapted from the literature procedure by Okujima et al.$^{19}$ Compound 34 [sodium 2-bromoethanesulfonate] (10.6 g, 50 mmol) was dissolved in pyrrolidine (50 mL) in a 100 mL round-bottom flask equipped with a stir-bar. The solution was heated to 50 °C and stirred overnight. The reaction was then condensed under reduced pressure and was added to diethyl ether while stirring. The precipitate was then collected using vacuum filtration and dried under reduced pressure to yield a white amorphous solid (7.6 g, 76% yield) $^1$H NMR (400 MHz, D$_2$O) $\delta$ 1.76 (4 H), 2.57 (4 H), 5.0d 2.89 (2 H), 3.07 (2 H).
4.7 References.


Chapter V

Molecular Organometallic Resists for EUV (MORE)

5.0 Overview.

Chapter V focuses on the development of a novel system of photoresists for EUV, which we have named Molecular Organometallic Resists for EUV (MORE). The goal of this work is to use elements with high EUV optical-densities to create high-sensitivity, high-resolution photoresists capable of meeting the needs of the 10-nm lithography node. Over the course of this work we investigated compounds made from Zn, Sn Cr, Fe, Co, Ni and Cu. For each element, we synthesized a series of potential MORE compounds and evaluated each compound for solubility, coating quality and lithographic sensitivity. An overview of results is listed below.

- **Solubility.** Some compounds we tested were not soluble in organic solvents. We have analyzed the insoluble materials and made predictions for the cause of these solubility issues.

- **Coating Quality.** Many of the compounds we tested formed poor quality films. Over the course of this work, we observed films that do not wet the wafer, form inhomogeneous film thicknesses, and crystallize on the wafer. It is important for a resist film to be homogeneous and amorphous to prevent light scattering and to get good imaging results.

- **Lithographic Sensitivity.** The compounds we tested had large variations in EUV sensitivities, ranging from 3 to over 1000 mJ/cm².
Our initial plan was to screen a broad range of materials, and to then focus on the most promising compounds. Through this screening, we selected tin-based materials and transition-metal oxalates for a more rigorous testing.

5.1 Introduction.

As stated in section 1.6.2, as resolution is improved, resist film thicknesses must decrease, however, there are a number of challenges associated with organic thin-resist films.

**Etch Resistance.** The ultimate purpose of a photoresist is to protect the underlying substrate from an etch process. As the microelectronics industry improves resolution, the resist film thickness must concomitantly decrease to prevent pattern collapse. Organic-resist film thicknesses are near the limits of being able to protect the substrate from the etch process.\(^1,2\) We predict the etch-processing of thin-organic films will not be capable of meeting the needs of future lithography nodes.

**Resolution Approaching the Polymer Radius of Gyration.** As resolutions improve, the sizes of patterned features in resist films are approaching the radius of gyration of the resist polymers (~1 to 5 nm).\(^3\) At these resolutions, the patterned features appear to be composed of discreet components rather than a continuous film, degrading LER. In future technology nodes, we predict LER improvements will be incapable of exceeding the size of individual polymer segments, and thus not meet future LER goals.\(^4,6\)
Resolution Approaching the Acid Diffusion Length. One of the biggest challenges today with chemically amplified systems is the control of acid diffusion. If photoacid created in the exposed region diffuses into the unexposed region, image contrast is lost.\textsuperscript{7} We predict that as resolutions continue to improve, the control of photoacid diffusion required to print the small features needed by the semiconductor industry, will not be possible.

Optical Density. The optical density of carbon is relatively low in EUV.\textsuperscript{8} As film thickness decreases, the amount of absorbed dose will also decrease.\textsuperscript{9} Even the darkest polymer films are incapable of absorbing more than \(\sim 30\%\) of the light at 20-nm film thicknesses. This low film optical density ultimately results in a poor sensitivity due to the inefficient absorption of photons.

In order to overcome many of the problems discussed for organic polymer resists, we have developed a novel class of inorganic resists which we have named Molecular Organometallic Resists for EUV (MORE). MORE is a class of photoresist materials made from inorganic or organometallic compounds or clusters which are chosen from high OD metals throughout the periodic table. We predict that MORE materials will have significant benefits over organic polymer systems.
• **High EUV Optical Density.** Since some metals in the periodic table are greater than ten times darker than carbon, highly absorbing resist films can be made.

• **High Mass Density.** Inorganic films typically have a mass density 5-10X greater than polymer films. By increasing the mass density of the resist films, image blur caused by secondary electron generation should be reduced.

• **Excellent Etch Rates.** The etch process typically involves the reaction of radical fluorine with both the resist and substrate. Carbon and silicon tetrafluorides are volatile gasses, resulting in the low etch selectivity of organic resist films on silicon substrates. Most metal fluorides are solids at room temperature, and so we predict MORE resists to have significantly better etch selectivity than organic resists.

• **No Acid Diffusion.** Since these films are not chemically amplified, photoacid diffusion is not a concern.

• **High Non-Chemically Amplified Reactivity.** We predict that by tuning the reduction/oxidation potential of the metals, high-sensitivity non-chemically amplified systems can be made.

**Selection of MORE Materials.** To identify the high EUV optical density elements, the optical density for all elements on the periodic table was calculated at standard state density and compared to carbon (Figure 5.1). Elements were then selected based on optical density, cost, toxicity and radioactivity. Through the remainder of this chapter, the synthesis and lithographic evaluation of compounds made from Zn, Sn Cr, Fe, Co, Ni and Cu will be discussed.
Figure 5.1. The EUV optical density at standard-state density was calculated for all elements on the periodic table and then compared to carbon. The periodic table has been color coded for easy identification of high optical density elements.\(^8\)
Through the work in this chapter, we plan to address a number of questions we have developed about Molecular Organometallic Resists for EUV (MORE):

- Can inorganic/organometallic compounds act as photoresists?
- How do different metals affect performance?
- How does ligand structure affect performance?

5.2 Survey of Simple Metal Complexes.

To better understand the challenges faced by MORE, a large survey of simple metal complexes was tested. There are very few literature examples of films made by spin-coating inorganic or organometallic molecules and no examples of EUV sensitivity. We started the work on MORE by performing a survey of simple metal complexes with the goal of answering the following questions:

- Will inorganic and organometallic compounds form high-quality, amorphous films?
- Will thin metal-containing films of MORE compounds be air stable?
- Will ligand decomposition in MORE films cause significant outgassing?

We purchased or made a large series of simple inorganic complexes (i.e. transition metal diketonates, zinc carboxylates and metal halides) and tested them as resists. We found that although many of the materials tested formed poor quality films due to crystallization, precipitation and non-wetting of the wafer, some of the materials formed good-quality, air-stable, amorphous
films. The materials that coated well were tested at Paul Scherrer Institut (PSI) in Switzerland, and were found to have little outgassing, but also poor sensitivities.

We predict the tested MORE complexes have poor sensitivities due to the stability of the ligands. From these initial results, we concluded that in order for MORE compounds to have good sensitivities, not only do photons need to be absorbed, but the ligands must be designed to undergo photolytic decomposition.

5.3 Tin Compounds.

Tin compounds have myriad literature examples, high EUV optical densities and low oxidation potentials, making them ideal candidates for MORE. Although the tin literature is vast, there exist few examples involving photochemistry and none involving exposure to EUV light. The goal of this work is to investigate tin compounds as candidates for MORE through the exploration and modification of known tin complexes.

Here we present two categories of materials which we have investigated for EUV sensitivity: Sn-1 compounds and Sn-12 clusters. The Sn-1 compounds contain a single tin atom, with four, potentially photoactive, ligands. The Sn-12 clusters are oxoclusters containing twelve tin atoms found to undergo EUV photochemistry in our preliminary trials, and for which we have investigated possible exposure reactions. This section will describe the preliminary syntheses and results for both material types.
5.3.1 Sn-1 Compounds.

**Initial Designs of Sn-1 Compounds.** Due to the known photochemistry of metal oxalates, early investigations into Sn-1 compounds focused on the development of tin oxalates, but these compounds were found to have poor solubility. Tin dioxalate has been used as a polymerization initiator and crosslinker, but is also extremely insoluble.\(^{10-12}\) To find a more soluble tin oxalate, we investigated organotin oxalate complexes with soluble, lipophilic organic groups. One patent reported the synthesis of dibutyltin oxalate *via* the hydrolytic exchange reaction between the commercially available dibutyltin oxide and oxalic acid.\(^{13}\) We repeated this reaction, and found an insoluble solid was produced. To confirm this insolubility, we repeated the synthesis through an alternate tin hydride pathway.\(^{14}\) Tin hydrides are known to react with carboxylic acids to yield tin carboxylates and elemental hydrogen.\(^{15}\) Dibutyltin dihydride was synthesized by a previously published route.\(^{16}\) When the dihydride was combined with oxalic acid, an insoluble white precipitate was formed. Due to the insolubility of products from both reactions, we think dibutyltin oxalate is too insoluble for use (Figure 5.2A).

**Development of Sn-1 Solubility Hypothesis.** Through experimentation with alternate Sn-1 compounds, we developed a hypothesis on solubility. Three other Sn-1 compounds were synthesized using formic acid, catechol and \textit{tert-}butyl catechol. The catechol complex, like the oxalate complex, is insoluble.
The tert-butyl catechol complex is a semi-soluble solid, and the formic acid complex is a semi-crystalline solid with excellent solubility in organic solvents (Figure 5.2B). We hypothesize these tin compounds form 6-coordinate complexes which can dramatically affect solubility. The dibutyltin oxalate is constrained to a 4-coordinate complex, allowing intermolecular coordination, ultimately resulting in the formation of an insoluble network structure. The dibutyltin diformate however, can orient itself such that the carbonyl oxygens are coordinating with the tin, preventing crosslinking and resulting in a significantly more soluble product (Figure 5.2C).
Figure 5.2. Synthesis of four Sn-1 clusters. (A) Two synthetic pathways to create the dibutyltin oxalate both resulted in an insoluble precipitate. (B) Four Sn-1 clusters were synthesized, of which, only one had good solubility properties, most likely due to the formation of a 6-coordinate tin. (C) The lone-pair carbonyl electrons can reach around, forming a soluble monomeric structure for the dibutyltin diformate. The lone-pair electrons on the oxalate, however, are constrained from intramolecular rearrangement to fill the empty tin binding sites. This forces intermolecular coordination to occur, resulting in an insoluble, network structure.
Sn-1 Solubility Hypothesis and Preliminary Lithographic Evaluations.

In order to test our Sn-1 solubility hypothesis and to evaluate EUV photosensitivity, eleven Sn-1 compounds were synthesized and evaluated (Figure 5.3). The trend in solubility appears to correlate with our theory; all compounds that are capable of forming 6-coordinate intramolecular structures are significantly more soluble than those that cannot. Compounds 36, 37, 38, 40, 41 and 42 all form products with poor solubility and we were unable to coat these materials. Although soluble, compounds 43 and 44 formed highly crystalline films and were not exposed. Compound 45 formed a good, amorphous film, however no photosensitivity was observed.

Compounds 39 and 46 both formed good stable films which were capable of imaging. Compound 39 resolved 50 and 35 nm HP lines at a dose of 50 mJ/cm²; smaller resolutions appeared to image, but with poor image quality. Compound 46 resolved better resolutions, down to 18 nm HP lines, but at a worse sensitivity of 190 mJ/cm².
**Figure 5.3.** Eleven Sn-1 compounds made and tested with some general results. Most of the compounds were unable to form quality films, due to poor solubility or high crystallinity. Of the four compounds that formed good quality films, two gave imaging results; one imaging 18-nm lines.

**Probable Mechanism for Sn-1 Cluster Photolysis.** When designing these systems, we used sets of materials capable of undergoing two different mechanisms: reductive elimination and decarboxylation. We predicted that some of the materials might undergo the reductive elimination of two ligands, resulting in the formation of the Sn(II) compounds. Sn(II) compounds are
unstable in air and will quickly oxidize to the Sn(IV) oxide, which is very insoluble. Since compound 45 did not appear to be photosensitive, we do not think reductive elimination is occurring. A second mechanism that we predict may occur is photolytic decarboxylation.\textsuperscript{17-22} The decarboxylation mechanism is similar to the mechanism shown for PMMA in section 1.4.1.1. Homolysis at the carbonyl would result in the radical carboxylate, which could undergo oxidation to generate CO\textsubscript{2}. Hossenlopp \textit{et al.} has observed the loss of CO\textsubscript{2} in the similar system of dibutyltin diacetate at 230-nm excitation.\textsuperscript{22} Both compounds 39 and 46 could undergo decarboxylation reactions, converting a tin-ester group to a tin-hydride or alkyltin group.

\textbf{Figure 5.4.} Two possible photolysis mechanisms for Sn-1 compounds. (A) Reductive elimination would result in the reduction of the tin and loss of two ligands. (B) Decarboxylation would result in the loss of carbon dioxide and the possible recombination of radicals.
Although these Sn-1 materials show promise, issues with solubility, crystallinity and sensitivity need to be addressed. Okawara et al. studied the thermal decarboxylation of similar compounds and found the decarboxylation of phenyltin esters occurs much more readily than butyltin esters. By designing new Sn-1 compounds with substituted aromatic groups, and altering the aromatic (R1) and carboxylic (R2) substituents, we predict the solubility, sensitivity and crystallinity can be significantly improved (Figure 5.5).

![Synthetic route to improved Sn-1 compounds.](image)

**Figure 5.5.** Synthetic route to improved Sn-1 compounds.

### 5.3.2 Sn-12 Clusters.

Sn-12 clusters of the type \[(RSn)_{12}O_{14}(OH)_{6}]X_2\] have been studied for over 20 years.\(^{24-60}\) The structure of these clusters consists of a spherical tin-oxide cage, with each tin covalently bound to one organic (R) group. The cluster is cationically charged (+2) and so is bound by two charge-neutralizing anionic ligands (X). These materials have been investigated as self-assembled monolayer dopants,\(^{54}\) as esterification catalysts\(^{56}\) and as organometallic hybrid materials,\(^{57}\) but as of yet their photochemistry has not been explored.
Here we describe the synthesis and lithographic evaluation of tin-oxide clusters as MORE resists. Two series of Sn-12 clusters were made, varying the structure of the anionic ligand (X) and organic group (R). Both material sets were then evaluated lithographically using the PSI EUV interferometer and the results were analyzed.

As a preliminary test of the photochemical activity of tin clusters, compound 48 was made by a previously reported method (Figure 5.6), spin-coated and tested for EUV sensitivity through a pinhole exposure using the Berkeley DCT. After exposure and development, an image was made and examined by an optical microscope. Although the film quality of the exposed region was relatively poor, it indicated that the cluster did undergo a change in solubility due to EUV exposure with a reasonable dose of 20 mJ/cm².
Figure 5.6. Modified synthetic pathway for tin clusters used in anionic ligand decomposition study. (a) p-toluenesulfonic acid and toluene reflux, 48 hrs (b) tetrabutylammonium hydroxide in isopropanol, crystallize at -15 °C (c) Tetrahydrofuran and carboxylic acid, evaporate under reduced pressure.43,50

Since a change in solubility during exposure was observed, some change in chemical structure or physical structure of the film must occur. In close examination of the structure, we have identified two possible mechanisms for this change in solubility: the anionic ligand decomposition and homolytic cleavage of the tin-carbon bond. In order to better understand this photochemical change, each possible pathway was isolated and examined through structural variation.
**Anionic Ligand Decomposition.** As stated previously, each cluster is composed of a +2 cationic core bound by two charge-balancing anionic ligands. We hypothesize that one possible mechanism for the observed photosensitivity of these clusters is a photolytic decomposition of the anionic ligands. Similar to the decarboxylation mechanism suggested for the Sn-1 compounds (section 5.3.1), homolysis of the carbonyl could result in the generation of a radical carboxylate, followed by the loss of CO₂ and reduction of the tin-oxide core (Figure 5.7). Since this mechanism involves the breaking of a bond, the relative sensitivity of these clusters should correlate directly with bond energy.

\[
\begin{align*}
\text{phenylacetate} & \xrightarrow{hv} \text{benzyl radical + carboxylate} \\
\end{align*}
\]

**Figure 5.7.** Photo-induced homolytic cleavage of phenylacetate. Phenylacetate is known to undergo a photochemical decarboxylation where generation of benzyl radical has been detected suggesting a homolytic cleavage mechanism.¹⁷,¹⁸,²⁰,²¹,⁶²

In order to test the effect of the ligand structure, a series of clusters with different anionic ligands were made. In 1998, Eychenne-Baron et al. reported on the synthesis of compound 49.⁴³ With this compound, there are several literature examples of people adding stoichiometric acid (HX) to quench the hydroxide and produce the desired cluster \([(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6] X_2\).⁴¹,⁵⁰,⁵⁷ Five carboxylic acids were selected for this study, with bond dissociation
energies ranging from 67 to 103 kcal/mol (Table 5.1). Each acid was then combined with a stoichiometric amount of tin cluster 49 to produce the corresponding clusters 50 through 54.

<table>
<thead>
<tr>
<th>Acid (HX):</th>
<th>Structure:</th>
<th>Bond Dissociation Energy (kcal/mol):</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(BuSn)_12O_14(\text{OH})_6][CH_3CH_2COO_] _2</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>[(BuSn)_12O_14(\text{OH})_6][\text{OCOCOO} ] _2</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>[(BuSn)_12O_14(\text{OH})_6][\text{OCOCH}_2\text{COO} ] _2</td>
<td>85*</td>
<td></td>
</tr>
<tr>
<td>[(BuSn)_12O_14(\text{OH})_6][\text{HCOO} ] _2</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>[(BuSn)_12O_14(\text{OH})_6][\text{C}_3\text{H}_5\text{COO} ] _2</td>
<td>103</td>
<td></td>
</tr>
</tbody>
</table>

* Bond energy estimated from bond energy of acetic acid 0-proton.

**Table 5.1.** Five tin clusters were synthesized by combining the appropriate acid (HX) with the tin cluster hydroxide (49). The relative bond energy for each acid is also included and, if decomposition occurs, should correspond with the relative sensitivity.63

Clusters 50 through 54 were coated on wafers and tested lithographically. In lithography, the sizing dose (ESize) is frequently used as an indicator of resist sensitivity and is defined as the dose at which the dimensions of the mask are directly translated to the resist. For the purposes of this study, ESize is the dose at which 50-nm lines are printed for the 50-nm HP pattern. ESize was determined for clusters 50 through 54 and their relative sensitivities were compared (Figure 5.8).
Figure 5.8. Tin clusters of the type [(BuSn)₆O₁₄(OH)₆]ₓ were investigated lithographically and the relative sensitivity (E_{size}) was determined for each.

Comparison of bond dissociation energy and E_{size} led us to a change in the predicted mechanism. When bond dissociation energy was compared with E_{size}, no correlation was observed (Figure 5.9A). We did notice a correlation between ligand molecular weight and E_{size}: E_{size} increases proportionally with the molecular weight of the anion (Figure 5.9B). Our interpretation of this data is that the photoreaction occurs with the tin-oxide cation rather than the anionic ligand, and the anionic ligands only act as non-reactive spacers inhibiting the clusters from combining.
Figure 5.9. (A) Bond dissociation energy vs. \( E_{\text{Size}} \) does not show any correlation. (B) Ligand molecular weight vs. \( E_{\text{Size}} \) shows a direct correlation. These results suggest a mechanism involving the cluster core, not the anionic ligands.

**Homolytic Cleavage of the Tin-Carbon Bond.** A second possible reaction that could occur during exposure is homolytic cleavage of the tin-carbon bond. Tin-carbon bonds are relatively weak (~50 kcal/mol), and tin forms extremely stable radicals, therefore it is conceivable that EUV exposure could cause homolysis.\(^6\) If homolysis occurs, we predict that stabilizing or destabilizing the organic radical should result in a change in the photosensitivity of the cluster. Figure 5.10 shows a series of organic groups with their associated C-H bond dissociation energy. The bond dissociation energy of the C-H bond should directly correlate with the relative radical stability of the organic group. The goal of this study was to synthesize a series of Sn-12 clusters containing alkyl groups with different radical stabilities, and to then test these clusters for sensitivity and imaging.
Figure 5.10. The bond dissociation energies for three organic groups. By incorporating these groups into the Sn-12 clusters, a broad distribution of Sn-C bond energies should be achieved.63

Few literature examples involve the synthesis of Sn-12 clusters with alkyl groups other than butyl, none with allyl or phenyl groups, so an exploration of the Sn-12 synthesis was necessary. Sn-12 clusters have been synthesized by either the dehydration of butylstannoic acid,43 or the controlled hydration of butyltin trichloride,59 butyltin trialkoxide35 or butyltin trialkyne.42 Since butylstannoic acid is generally made by rapid hydrolysis of butyltin trichloride, our starting material targets were alkyltin trichlorides.59 Allyltin trichloride was synthesized through a previously published route, phenyl and butyltin trichlorides were purchased.65 Our first attempts to synthesize the Sn-12 clusters involved converting the organotin trichloride to the organostannoic acid, followed by dehydration to make the cluster (Figure 5.11A). Initial attempts with phenyltin trichloride, however, only yielded an insoluble white solid which is thought to be tin(IV) oxide (due to hydrolysis of the phenyl-tin bond). Several hydrolysis methods were subsequently attempted, and hydrolysis
of the organotin trichloride using ammonium hydroxide proved the most successful route (Figure 5.11B). The reaction product is a soluble polymeric material which has similar size to the Sn-12 cluster by gel permeation chromatography (GPC). All attempts to crystallize the clusters were unsuccessful and so the unpurified products were lithographically evaluated. The predicted structures (allyl (55), butyl (56) and phenyl (57)) are shown in table 5.2.

**Figure 5.11.** Synthesis of the Sn-12 clusters. (A) Initial attempts to synthesize the clusters by the conversion of phenyltin trichloride to phenylstannanoic acid followed by dehydration failed. (B) Hydrolysis of phenyltin trichloride using ammonium hydroxide produces a soluble polymeric material which we think is the Sn-12 cluster.
Table 5.2. Three tin-oxide materials (allyl, butyl, phenyl) were made from the hydrolysis of the corresponding organotin trichloride.

<table>
<thead>
<tr>
<th>Tin Trichloride Precursor:</th>
<th>Structure:</th>
<th>C-H Bond Dissociation Energy (kcal/mol):</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 55" /></td>
<td>(55) [(H_2C=CHCH_2Sn)]<em>{12}O</em>{14}(OH)_{6}Cl_2</td>
<td>88</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 56" /></td>
<td>(56) [(BuSn)]<em>{12}O</em>{14}(OH)_{6}Cl_2</td>
<td>101</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 57" /></td>
<td>(57) [(PhSn)]<em>{12}O</em>{14}(OH)_{6}Cl_2</td>
<td>113</td>
</tr>
</tbody>
</table>

Clusters 55 through 57 were coated on wafers and tested lithographically (Figure 5.12). Clusters 55 and 56 showed poor image quality, likely attributed to impurities. Due to the poor image quality, it was difficult to accurately measure line-widths for the imaged patterns and so the dose approximately at $E_{\text{size}}$ was used. Figure 5.13 shows the C-H bond energy vs. dose curve for clusters 55 through 57. The dose of these clusters appears to correlate directly with C-H bond energy which supports the mechanism of tin-carbon bond homolysis.


**Figure 5.12.** The lithographic results for three tin clusters containing different organic groups.

<table>
<thead>
<tr>
<th>R:</th>
<th>Allyl</th>
<th>Butyl</th>
<th>Phenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 nm Lines:</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Dose (mJ/cm²):</td>
<td>180</td>
<td>280</td>
<td>510</td>
</tr>
</tbody>
</table>

**Figure 5.13.** Bond Energy vs. Dose. 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 which suggests a homolysis is occurring.
**Interpretation of Results.** The results of studying both the anionic ligand (L) and organic group (R) suggest an exposure mechanism of tin-carbon bond homolysis. If exposure resulted in homolytic cleavage of the tin-carbon bond, the tin radical could then recombine with another adjacent tin radical resulting in agglomeration of the clusters. Large anionic ligands could interfere with this tin-tin bond formation, decreasing the probability of cluster agglomeration and decreasing the resist sensitivity. This mechanism is supported by thermogravimetric analysis (TGA) data. Eychenne-Baron *et al.* reported a loss of ~25 % mass which they attributed to the thermal loss organic groups.$^{52}$

**5.4 Metal Oxalate Complexes.**

Transition metal oxalates are a class of compounds with known photochemical reactivity at wavelengths longer than EUV (UV/Visible), and so were investigated as MORE materials. The thermal and photochemical reaction of transition metal oxalates has been thoroughly studied in the literature.$^{62,66,67}$ The oxalate decomposes, generating two molar equivalents of carbon dioxide, and reduces the metal by two electrons (Figure 5.14).
Figure 5.14. The photolytic decomposition of transition metal oxalates. Upon exposure, the oxalate ligand decomposes, producing two molar equivalents of carbon dioxide.

Over the course of the last 100 years, the synthesis of different transition metal oxalate complexes has been thoroughly investigated. In this section, we will investigate the lithographic properties of a series of different transition metal oxalates of the structure [ML₃]Xₙ, where M is a transition metal, L is a bidentate ligand and X is a charge-balancing counter-ion. To better understand the lithographic properties of this series of MORE compounds, we studied three properties of these materials through structural variation: ligand structure, central metal and oxalate loading.

5.4.1 Ligand Structure.

In the literature, transition metal oxalates have been made with a variety of different ligands. We predict the physical properties of the film may be closely related to the structure of the ligands bound to the metal. To investigate the effect of ligand structure, we chose three amine/imine ligand-types (L): ethylenediamine (en), 2,2’-bipyridine (bpy) and phenanthroline (phen). For each ligand-type, compounds of the form L₂Co(oxalate)•PF₆ were made and evaluated. Compounds containing en (58) and phen (60) ligands were found to be insoluble in common solvents (Figure 5.15). Compound 59, containing the bpy ligand, has good solubility in polar solvents such as acetonitrile.
Figure 5.15. Three cobalt-oxalate complexes containing the amine/imine ligands: en (58), bpy (59) and phen (60). For the three ligands shown, only the bpy ligand forms soluble adducts.

5.4.2 Central Metal.

In order to investigate different material sets, we compared the reactivities of several transition-metal oxalate complexes to EUV exposure. Many of the transition metals form similar oxalate complexes, yet have different oxidation states, oxidation potentials and EUV optical densities. By investigating similar transition-metal complexes containing different metal centers, we can better evaluate and understand the trends of these systems.

Complexes containing Cr, Fe, Co, Ni and Cu were made and tested for EUV exposure at the PSI interferometer. Ni and Cu metals form 4-coordinate complexes, and these materials were found to have poor solubility in common solvents.\textsuperscript{74,75} We hypothesize this poor solubility may be due to the
intermolecular coordination of the metal of one molecule and the carbonyl oxygen of one or more other molecules. Cr, Fe and Co metals form soluble 6-coordinate structures and have good imaging capabilities, all able to resolve 35 nm HP lines (Figure 5.16).\textsuperscript{69,71,73} The relative reactivity of the metal centers appears to go Cr < Fe < Co, which directly correlates with the relative optical densities of the metals.

![Figure 5.16](image)

**Figure 5.16.** Three, 6-coordinate structures were made and tested at the PSI interferometer. The relative reactivity of these three metal centers appears to correlate directly with the optical density: Cr < Fe < Co.

### 5.4.3 Oxalate Loading.

To understand what role the oxalate plays in the sensitivity of transition metal oxalates, a series of cobalt complexes were studied, varying the ratio of oxalate to bpy.\textsuperscript{68,71,76} Four compounds were made and tested using the Berkeley Dose Calibration Tool (DCT).\textsuperscript{61} Each material was coated, exposed, optimized for develop and $E_{\text{max}}$ was measured (Figure 5.17). $E_{\text{max}}$ is defined as
the lowest dose where no film loss is observed, and is commonly used as a sensitivity metric for negative-tone resists. Comparing the four materials, the sensitivity improves by several orders of magnitude as oxalate loading is increased, improving from over 1400 mJ/cm² down to 3 mJ/cm².

![Image](image.png)

**Figure 5.17.** Four cobalt complexes were studied, each with a different ratio of oxalate to bpy. Oxalate was found to have significant effects on the sensitivity, improving $E_{\text{max}}$ from over 1400 mJ/cm² down to 3 mJ/cm².

### 5.4.4 Optimization Studies and Champion Results.

To better understand and evaluate the capabilities of transition metal oxalates as MORE materials, the best functioning material, compound 63, was optimized lithographically. Over the course of this work, 43 transition metal oxalates were tested. Compound 63 showed the best overall preliminary performance, and so the optimization of the lithographic properties was study. Compound 63 was coated at a 40-nm film thickness, exposed at 20 mJ/cm², and tested at different bake temperatures, as shown in Figure 5.18. A PAB of 90 °C appears to have little effect on the lithographic performance of Compound 63, where as a PEB of 90 °C causes a significant amount of image degradation.
Figure 5.18. A bake study was performed on Compound 63. A PAB of 90 °C appears to have little effect on the image performance, however a PEB of 90 °C causes a significant amount of LER.

The optimized imaging of compound 63 was reevaluated at thinner film thicknesses to prevent pattern collapse. At a film thickness of 40 nm, pattern collapse occurred for features smaller than 25 nm. To further optimize this system and prevent pattern collapse, a thinner film of compound 63 was evaluated. At a film thickness of 30 nm, compound 63 was evaluated using a PAB of 90 °C and no PEB and a dose of 30 mJ/cm². Compound 63 imaged down to 18 nm HP features; the smallest feature on the mask.
Figure 5.19. The thickness of compound 63 was decreased to 30 nm and reimaged. At this thin film thickness, 18-nm HP lines were imaged at the low dose of 30 mJ/cm².

5.5 Summary and Conclusions.

During the course of this work, a number of questions were investigated about Molecular Organometallic Resists for EUV (MORE):

**Can inorganic/organometallic compounds act as photoresists?**

Novel inorganic/organometallic resists have been made from elements with high EUV optical densities (Zn, Sn, Cr, Fe, Co, Ni and Cu).

- **Simple Metal Complexes.** Simple metal complexes, including transition metal diketonates and zinc carboxylates, were tested and found to have poor sensitivities to EUV. Our interpretation of these results is that in order for MORE resists to have good sensitivities, not only do photons need to be absorbed, but the ligands must be designed to undergo photolytic decomposition.
• **Sn-1 Compounds.** A series of dibutyltin compounds (Sn-1) were made and tested. All Sn-1 compounds that formed 4-coordinate complexes had poor solubility, which we hypothesize is due to intermolecular coordination of the tin, forming insoluble network structures. Some 6-coordinate complexes formed good films and were tested lithographically. Both dibutyltin carboxylates tested produced imaging, one able to resolve 18-nm HP lines. We reason the Sn-1 compounds undergo a decarboxylation reaction upon exposure, which agrees with 230-nm excitation data.

• **Sn-12 Clusters.** Tin clusters (Sn-12) of the structure [((RSn)_{12}O_{14}(OH)_{6})X_{2}] were investigated for EUV sensitivity. A series of Sn-12 clusters with varying anionic ligand (X) decarboxylative bond-energies were synthesized and evaluated for EUV imaging capabilities. The relative sensitivities do not appear to correlate with bond energies, but rather with ligand molecular weight. A series of Sn-12 clusters were then made varying the organic (R) group bound to the tin. Although we were unable to purify these materials by crystallization, the unpurified products were tested and the resist sensitivity observed correlates directly with the C-H bond energy of the organic (R) group. The results of both studies appear to indicate a homolytic-cleavage photolysis mechanism, where the tin-carbon bond is homolytically cleaved generating the tin radical, followed by formation of the tin-tin bond by radical recombination.

• **Transition-Metal Oxalates.** The effect on lithographic properties of changing the ligand structure, central metal and oxalate loading of transition-metal oxalates was evaluated. To test what effect changing the ligand structure has on resist properties, Co-oxalate complexes with en, bpy and phen ligands were made and only the bpy complexes were found to have good solubility properties. To test what effect changing the central metal has on resist properties, a series of Cr, Fe, Co, Ni and Cu compounds were made and evaluated lithographically. The Ni and Cu complexes formed insoluble,
4-coordinate structures. The Cr, Fe and Co compounds all formed soluble 6-coordinate compounds and the relative reactivity for these metals was Cr < Fe < Co. To test what effect changing the oxalate loading has on resist properties, a series of Co-complexes were made with ratios of 3:0, 2:1, 1:2, and 0:3 bpy to oxalate. The sensitivity of these materials ranged from over 1400 mJ/cm² (3:0 bpy:oxalate) to 3 mJ/cm² (0:3 bpy:oxalate), indicating the importance of the oxalate ligand. Finally an optimization study was performed on Compound 63, and 18-nm lines at a dose of 30 mJ/cm² were imaged.

**How do different metals affect performance?**

We hypothesize that EUV optical density as well as available oxidation states dictate the EUV sensitivity in MORE resists. Throughout these studies, we have investigated seven metals (Zn, Sn, Cr, Fe, Co, Ni and Cu) with varied results. We predicted that by increasing the film optical density, the resist sensitivity should improve. Within the transition-metal oxalates studied, we found the resist sensitivity correlates directly with optical density (Cr < Fe < Co). Of the metals tested, Sn has the highest EUV optical density, but all the tin compounds tested had worse sensitivities than the transition-metal oxalates. We predict this discontinuity is a result of the metal oxidation state. The transition metals Cr, Fe and Co were all tested in the +3 oxidation state, and are capable of being either oxidized or reduced. Sn was tested at the +4 oxidation state, the highest oxidation state for Sn and so only reduction can occur. The mechanism for EUV exposure discussed in section 1.3 involves the photo-induced oxidation of the polymer generating a secondary electron which ultimately reduces a PAG. If a similar mechanism were assumed for the
MORE systems, the transition-metal oxalates can be both oxidized and reduced, resulting in the possible generation of an electron cascade and resulting in the reaction of multiple compounds per photon. (Figure 5.20A). The Sn resists cannot oxidize, and so would not benefit form an electron cascade and resulting in only one reaction per absorbed photon (Figure 5.20B).

**Figure 5.20.** The possible mechanism of MORE compounds. (A) Exposure of the transition-metal complexes could result in an electron cascade, where a photon is absorbed causing secondary electrons to be expelled into the film. Upon expulsion, the secondary electrons can then catalyze the extraction of more secondary electrons or recombine with another transition-metal complex, resulting in the turn-over of several chemical reactions per photon. (B) Since Sn(IV) can only be reduced, a similar electron cascade is unlikely, resulting the a turn-over of only one chemical reaction per photon and ultimately, a poor sensitivity.
How does ligand structure affect performance?

The effect of ligand structure was studied for all systems.

- **Sn-1 Compounds.** We reason that Sn-1 compounds undergo a photo-induced decarboxylation reaction when exposed. Eleven Sn-1 compounds were made with different ligands, and we found that ligand structure has a strong influence on solubility and photosensitivity. Ligands that allow intramolecular coordination form significantly more soluble complexes than ligands that do not. Phenol ligands do not form photosensitive complexes, whereas carboxylate ligands most likely undergo a photo-induced decarboxylation. The trichloroacetate ligand has worse sensitivity, but much better resolution than formate, with imaging down to 18-nm HP lines.

- **Sn-12 Clusters.** Sn-12 clusters of the structure [(RSn)\(_{12}\)O\(_{12}\)(OH)\(_6\)]X\(_2\) have two types of ligand: anionic ligands (X) and organic ligands (R). The effect on lithographic performance was evaluated for each of these ligand types through structural variation. The anionic ligands (X) do not appear to undergo photolysis, but rather act as unreactive spacers, separating the clusters and decreasing sensitivity based on ligand size. The organic ligands (R) appear to undergo homolytic cleavage, the cluster sensitivity correlating directly with the C-H bond strength of the ligands.

- **Transition-Metal Oxalates.** For the transition-metal oxalate systems, the effects of changing the ligand structure and the oxalate loading on resist properties were investigated. The effect of changing the ligand structure was evaluated by making similar cobalt-oxalate complexes with en, bpy and phen ligands and observing the relative solubility. The en and phen complexes have very poor solubility and cannot be spin-coated. The bpy complexe has good solubility in polar solvents such as acetonitrile. The effect of changing the
oxalate loading was investigated by making four similar cobalt-complexes with ratios of 3:0, 2:1, 1:2, and 0:3 bpy to oxalate. This set of compounds was evaluated lithographically, and the sensitivity ranged from over 1400 mJ/cm² (3:0 bpy:oxalate) to 3 mJ/cm² (0:3 bpy:oxalate), indicating the importance of the oxalate ligand.

5.6 Experimental Methods.

General. All reactions were carried out under a nitrogen atmosphere. The reagent butyltin hydroxide oxide was purchased from Alfa Aesar. Phenyltin trichloride was purchased from Gelest and all other reagents were purchased from Sigma Aldrich. 2-oxo-2-(phenylamino)-acetic acid was prepared by the literature procedure. Compounds 58 through 66 were prepared by the literature procedures. Pyridine and triethylamine were dried by distillation over potassium hydroxide pellets and stored under nitrogen with 4Å-molecular sieves. All other reagents were used as received unless otherwise specified.

Instruments. Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker 400 spectrometer. All chemical shifts are reported as parts per million (ppm) relative to residual proton peaks of the deuterated solvent.
General Synthetic Procedure for Compounds 36 through 46. Adapted from the literature procedures.\textsuperscript{78,79} Compound 67 (2.489 g, 10 mmol) was combined with 20 mmol of acid in toluene (20 mL) in a 50 mL round-bottom flask, equipped with a stir-bar and a Dean-Stark water trap. The flask was refluxed for one hour then the solvent was removed under reduced pressure. The crude material was crystallized if possible.

2,2-dibutyl-1,3,2-dioxastannolane-4,5-dione (36). Oxalic acid (0.904 g, 10 mmol) was used as the acid. The compound was unable to be crystallized or NMR performed due to solubility.

2,2-dibutylbenzo[d][1,3,2]dioxastannole (37). Catechol (1.101 g, 10 mmol) was used as the acid. The compound was unable to be crystallized or NMR performed due to solubility.

5-tert-butyl-2,2-dibutylbenzo[d][1,3,2]dioxastannole (38). tert-Butyl-catechol (1.662 g, 10 mmol) was used as the acid. The compound was found to be soluble only in refluxing pyridine and so was unable to be crystallized or NMR performed.
dibutylstannanediyl diformate (39). Formic acid (0.906 g, 20 mmol) was used as the acid. The compound was crystallized in hexane. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.30 (2 H), 1.63 (4 H), 1.46 (4 H), 1.35 (4 H), 0.89 (6 H).

2,2-dibutyl-1,3,2-dioxastannolane (40). Ethylene glycol (0.621 g, 10 mmol) was used as the acid. The compound was crystallized in hot toluene. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 3.60 (4 H), 1.61 (4 H), 1.34 (8 H), 0.89 (6 H).

(E)-2,2-dibutyl-5-(phenylimino)-1,3,2-dioxastannolane-4-one (41). 2-oxo-2-(phenylamino)- acetic acid (1.652 g, 10 mmol) was used as the acid. The compound was found to be soluble only in refluxing pyridine and so was unable to be crystallized or NMR performed.

2,2-dibutyl-1,3,2-dioxastannolane (42). Pinacol (1.182 g, 10 mmol) was used as the acid. The compound was crystallized in hot toluene. Appears to be a mixture of isomers by NMR (see Appendix).

dibutylstannanediyl bis(2-phenylacetate) (43). Phenylacetic acid (2.723 g, 20 mmol) was used as the acid. The compound was crystallized in hexane. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.26 (10 H), 3.64 (4 H), 1.56 (8 H), 1.24 (4 H), 0.78 (6 H).

dibutylbis(pyridin-2-ylthio)stannane (44). 2-mercaptopyridine (2.223 g, 20 mmol) was used as the acid. The compound was crystallized in hexane. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.08 (2 H), 7.42 (2 H), 7.30 (2 H), 6.90 (2 H), 1.60 (8 H), 1.30 (4 H), 0.89 (6 H).
dibutylbis(quinolin-8-yloxy)stannane (45). 8-hydroxyquinoline (2.904 g, 20 mmol) was used as the acid. The compound was crystallized in hexane. 

$^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.43 (2 H), 8.00 (2 H), 7.49 (2 H), 7.22 (2 H), 7.12 (2 H), 6.99 (2 H), 1.36 (4 H), 1.21 (4 H), 1.12 (4 H), 0.89 (6 H).

dibutylstannanediyl bis(2,2,2-trichloroacetate) (46). 2,2,2-trichloroacetic acid (3.268 g, 20 mmol) was used as the acid. The compound was crystallized in hexane. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 1.66 (8 H), 1.36 (4 H), 0.89 (6 H).

General Synthetic Procedure for Compounds 50 through 54. Compound 49 (1.0 g, 0.41 mmol) was dissolved in tetrahydrofuran (10 mL) in a 50 mL round-bottom flask equipped with a stirbar. Two molar equivalents (0.82 mmol) of a 10% solution by weight of acid dissolved in tetrahydrofuran was added and the flask was stirred for ten minutes. The solvent was removed by vacuum and the compound was used as is.
\[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6][\text{C}_6\text{H}_5\text{CH}_2\text{COO}]_2\] (50). Phenylacetic acid (0.112 g, 0.82 mmol) was used as the acid. $^1\text{H}$ NMR (400 MHz CDCl$_3$) $\delta$ 7.30 (4 H), 7.20 (4 H), 7.11 (2 H), 1.79 (12 H), 1.57 (24 H), 1.52 (12 H), 1.33 (12 H), 1.05 (12 H), 0.95 (18 H), 0.88 (18 H).

\[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6][\text{OC}O\text{COO}]\] (51). Oxalic acid (0.037 g, 0.41 mmol) was used as the acid. $^1\text{H}$ NMR (400 MHz CDCl$_3$) $\delta$ 1.76 (12 H), 1.61 (12 H), 1.54 (12 H), 1.48 (12 H), 1.32 (12 H), 1.06 (12 H), 0.94 (18 H), 0.87 (18 H).

\[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6][\text{OCOCH}_2\text{COO}]\] (52). Malonic acid (0.043 g, 0.41 mol) was used as the acid. $^1\text{H}$ NMR (400 MHz CDCl$_3$) $\delta$ 1.77 (12 H), 1.62 (12 H), 1.55 (12 H), 1.49 (12 H), 1.33 (12 H), 1.06 (12 H), 0.94 (18 H), 0.88 (18 H).

\[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6][\text{HCOO}]_2\] (53). Formic acid (0.038 g, 0.82 mmol) was used as the acid. $^1\text{H}$ NMR (400 MHz CDCl$_3$) $\delta$ 8.40 (2 H), 1.82 (12 H), 1.66 (24 H), 1.54 (12 H), 1.34 (12 H), 1.13 (12 H), 0.97 (18 H), 0.89 (18 H).

\[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6][\text{C}_6\text{H}_5\text{COO}]_2\] (54). Benzoic acid (0.100 g, 0.82 mmol) was used as the acid. $^1\text{H}$ NMR (400 MHz CDCl$_3$) $\delta$ 8.01 (4 H), 7.32 (6 H), 1.84 (12 H), 1.66 (24 H), 1.54 (12 H), 1.31 (12 H), 1.16 (12 H), 0.97 (18 H), 0.86 (18 H).
General Synthetic Procedure for Compounds 55 through 57. Water (20 mL) was placed in a 50 mL round-bottom flask equipped with a stir-bar and reflux condenser and nitrogen was bubbled through for ten minutes. The flask was placed under nitrogen and ammonium hydroxide (25% solution, 6.309 g, 45 mmol) was added to the flask as the flask was cooled using an ice bath. Organotin trichloride was quickly added to the flask while stirring, and the solution was refluxed for 30 minutes. Upon completion, the flask was cooled to room temperature and filtered through celite. The celite was washed twice with tetrahydrofuran, and the combined organic and aqueous solutions were extracted three times with ethyl acetate. The organic phases were combined, dried over sodium sulfate and condensed under reduced pressure. The crude oil was then dissolved in diethyl ether and precipitated with hexane to yield a solid. The solid was then dried under vacuum.

\[ \text{[(H}_2\text{C}=\text{CHCH}_2\text{Sn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2 \]  (55). Allyltin trichloride (3.992 g, 15 mmol) was used as the organotin trichloride. \(^1\text{H} \text{NMR} \ (400 \text{ MHz} \text{ CDCl}_3) \delta 6.13 \ (1 \text{ H}), 5.34 \ (1 \text{ H}), 5.30 \ (1 \text{ H}), 2.50 \ (2 \text{ H}).
[(BuSn)\(_{12}\)O\(_{14}\)OH\(_6\)]\(_2\)Cl\(_2\) (56). Butyltin trichloride (4.233, 15 mmol) was used as the organotin trichloride. \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta\) 1.84 (2 H), 1.79 (2 H), 1.72 (2 H), 1.63 (2 H), 1.52 (2 H), 1.81 (2 H), 0.97 (3 H), 0.88 (3 H).

[(PhSn)\(_{12}\)O\(_{14}\)OH\(_6\)]\(_2\) Cl\(_2\) (57). Phenyltin trichloride (4.533 g, 15 mmol) was used as the organotin trichloride. \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta\) 7.10 (5 H).

5.7 References.
9. The Beer-Lambert Law states the amount of total absorbed light is dependent upon the distance that light travels in an absorbing medium. With photoresist films, the distance the light travels is effectually the film thickness, therefore, the film thickness determines the total absorbed light or dose.


37. Constantin, D., Journal of Chemical Physics (2010) 133 (14), 144901/1


61. Dose Calibration Tool (DCT) - A tool designed and used at Lawrence Berkeley National Laboratories used in the dose calibration of a resist. The resist-coated wafer is placed in the tool and exposed with 50 separate exposures; each exposure at a different dose. The wafer is then processed and the film thickness vs. dose curves is typically measured.


64. Abel, E. W., *et al.*, *Comprehensive Organometallic Chemistry II*. Pergamon


76. Burstall, F. H., and Nyholm, R. S., *Journal of the Chemical Society (Resumed)* (1952), 3570


Appendix – Selected $^1$H NMR Spectra
Spectrum in D$_4$-Acetone

\[
[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Oxalate}
\]

51

Spectrum in D$_6$-Acetone

\[
[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Malonate}
\]

52
Spectrum in D$_2$-Acetone

[[BuSn]$_{12}$O$_{14}$(OH)$_6$][Formate]$_2$

Spectrum in D$_2$-Acetone

[[BuSn]$_{12}$O$_{14}$(OH)$_6$][Benzoate]$_2$
Spectrum in D$_6$-Acetone

\[\text{[(PhSn)$_{12}$O$_4$(OH)$_6$][Cl$_2$]}\]

57