Development of Inorganic Resists for Electron Beam Lithography: Novel Materials and Simulations

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Development of Inorganic Resists for Electron Beam Lithography: Novel Materials and Simulations

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Dedicated

to my father, Dr. Ayyamperumal Jeyaprakash,

to my mother, Margret Stella Packiam,

and to my grandparents.
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Electron beam lithography is gaining widespread utilization as the semiconductor industry progresses towards both advanced optical and non-optical lithographic technologies for high resolution patterning. The current resist technologies are based on organic systems that are imaged most commonly through chain scission, networking, or a chemically amplified polarity change in the material. Alternative resists based on inorganic systems were developed and characterized in this research for high resolution electron beam lithography and their interactions with incident electrons were investigated using Monte Carlo simulations. A novel inorganic resist imaging scheme was developed using metal-organic precursors which decompose to form metal oxides upon electron beam irradiation that can serve as inorganic hard masks for hybrid bilayer inorganic-organic imaging systems and also as directly patternable high resolution metal oxide structures. The electron beam imaging properties of these metal-organic materials were correlated to the precursor structure by studying effects such as interactions between high atomic number species and the incident electrons. Optimal single and multicomponent precursors were designed for utilization as viable inorganic resist materials for sub-50nm patterning in electron beam lithography. The electron beam imaging characteristics of the most widely used inorganic resist material, hydrogen silsesquioxane (HSQ), was also enhanced using a dual processing imaging approach with thermal curing as well as a sensitizer catalyzed imaging approach. The interaction between incident electrons and the high atomic number species contained in these inorganic resists was also studied using Monte Carlo simulations. The resolution attainable using inorganic systems as
compared to organic systems can be greater for accelerating voltages greater than 50 keV
due to minimized lateral scattering in the high density inorganic systems. The effects of
loading nanoparticles in an electron beam resist was also investigated using a newly
developed hybrid Monte Carlo approach that accounts for multiple components in a solid
film. The resolution of the nanocomposite resist process was found to degrade with
increasing nanoparticle loading. Finally, the electron beam patterning of self-assembled
monolayers, which were found to primarily utilize backscattered electrons from the high
atomic number substrate materials to form images, was also investigated and
characterized. It was found that backscattered electrons limit the resolution attainable at
low incident electron energies.
CHAPTER 1

1. INTRODUCTION AND BACKGROUND

The invention of the monolithic integrated circuit by Jack Kilby and Robert Noyce in 1958 spawned a revolution for integrating electronic components in a semiconductor substrate through internal connection amongst solid-state devices. Through the integration of active and passive device elements such as transistors, resistors, capacitors, and diodes, desired logical functions of an electrical circuit could be performed efficiently for developing semiconductor devices of high complexity. The small scale integration (SSI) of devices in the early history of integrated circuits (ICs) was observed to roughly double in terms of the number of integrated components about every two years by Gordon E. Moore which has been famously coined ever since as “Moore’s law”\(^1\). This empirical observation has provided an impetus for astonishing growth in the semiconductor industry that has been mainly achieved through miniaturization of devices for increased device component density per unit area. A historical plot of critical device dimensions and transistor density in Intel microprocessor units illustrates this remarkable growth (Figure 1-1)\(^2\). The physical dimensions of devices have shrunk from approximately 20 µm to the deep sub-µm regime while transistor density has increased by about five orders of magnitude. Furthermore, utilization of similar fabrication principles across several device generations has maintained the total manufacturing cost of an integrated circuit essentially constant over
the years. The complexity and design of semiconductor devices have also vastly evolved from miniaturization and integration. Microprocessors have progressed from 4-bit devices in the early 1970’s to the present day 32/64-bit state-of-the-art devices found in personal computers. Correspondingly, memory devices have also advanced from approximately 1 kbit capacities in the early 1970’s to the contemporary 1 Gbit dynamic random access memories (DRAM).

Figure 1-1: A historical plot illustrating the relationship in semiconductor manufacturing between minimum feature size and transistor density of integrated circuits in Intel microprocessor units.
A further consequence of the tremendous miniaturization in semiconductor devices is a concomitant enhancement of their performance. When considering the basic building block of an integrated circuit, a metal oxide semiconductor field effect transistor (MOSFET), scaling of physical dimensions, substrate doping, and swing voltages by a factor of $S$, $S$, and $1/S$, respectively, can result in enhancement of speed, reduction in power dissipation, and reduction in power delay product by a factor of $S$, $1/S^2$, and $1/S^2$, respectively (where $S>1$). The application of these simple scaling procedures enhances semiconductor device performance through miniaturization while the cost per functionality is decreased as more and more devices are built into a single integrated circuit. The device structure of the MOSFET has essentially remained unchanged over the years as the device dimensions have decreased through simple scaling procedures. Progressive miniaturization of MOSFET’s has been mainly achieved through reduction of its physical dimensions such as width and length. A key enabler of this tremendous shrinkage in semiconductor devices has been advancements in microlithography, which is the art of patterning thin film materials during the build up of a device. Advances in microlithography have sustained continual growth of the semiconductor industry by providing the capability of patterning the smaller and smaller device features required for increased device density. The remarkable progress in lithography is exemplified by critical patterning dimensions that have decreased by two orders of magnitude from the micron to the nanometer scale during just the past quarter century.
1.1. Lithographic Process

Fabrication of semiconductor devices necessitates patterning of selective regions for utilizing standard microelectronics processing steps such as etching, deposition, or ion implantation in the sequential build up of multiple layers of an IC device. The technique by which patterns are produced which physically distinguish or “mask off” the desired and undesired regions for further processing is referred to as “lithography”. The objective of the lithographic process is simply to cover and protect selected regions of the device during a particular processing step such that only the desired areas of the device are modified in any single processing step. To accomplish this objective, the lithographic process must: (1) provide a means to selectively protect certain regions of the device by producing a patterned masking material of the desired feature sizes which is commonly referred to as a “photoresist” and (2) produce a patterned photoresist mask that can survive the subsequent processing steps such as plasma etching and protect the underlying device from modification by these processes. After successful completion of a desired device build up process, the photoresist patterns are removed to resume further fabrication of the multilayer device. These lithographic processes are frequently repeated throughout the buildup of the device whenever selective processing is desired.

The basic steps involved in a lithographic process are illustrated schematically in Figure 1-2. Initially, the semiconductor silicon surface is chemically treated in a variety of chemical baths and cleaning steps that are designed to remove contaminants that may result in poor adhesion and defect formation in the photoresist film. The surface is often then further modified using an adhesion promoter which enhances the adhesion between
the device substrate and the photoresist. The photoresist is commonly a radiation
sensitive organic polymer that is used for defining the patterns and masking the device,
and it is referred to as a “photoresist” since it is “photo” sensitive and it “resists” chemical
and physical attack of the underlying substrate. Next, the photoresist is deposited onto
the silicon surface via spin coating from a solution containing the polymer dissolved in an
appropriate casting solvent. After film formation, the wafer is transferred to a hot plate
and baked at a temperature above the boiling point of the casting solvent in order to
remove excess solvent from the film and to thermally anneal residual stress in the film
built up during spin coating. This step is referred to as a post apply bake (PAB). Next,
the photoresist coated wafer substrate is typically irradiated with ultraviolet light through
a patterned mask containing the information that is to be transferred into the polymer.
The masked exposure causes chemical transformations in the exposed regions of the
photoresist which modulate the solubility of the exposed regions relative to the
unexposed regions of the photoresist in a developing solvent. After image formation, a
post exposure bake (PEB) step is often performed to either thermally anneal exposed
regions in order to reduce chemical gradients that may have been caused within the film
during the radiation exposure or to promote further chemical reaction in the exposed or
unexposed regions of the film. For example, during optical irradiation on reflective
substrates, standing waves are set up in the photoresist film which creates regions of
varying intensity within the thin film due to multiple reflections occurring at the resist–
substrate and resist–air interfaces which result in constructive and destructive optical
interference in the film. These regions of high and low light intensity within the film
result in differences in local photoreaction rates and thus create gradients in the chemical

composition of the film normal to the substrate. Such gradients are generally undesirable in microlithography since the desired chemical differentiation in the photoresist film is only across the plane of the film parallel to the substrate. Thermal baking can drive the diffusion of species within the resist film and can reduce or eliminate these gradients induced by standing waves. Also, some photoresists require a PEB to thermally activate and amplify chemical reactions in the exposed regions.

The dissolution behavior of the exposed polymer matrix in a solvent, such as a moderate aqueous base, is modulated by several orders of magnitude through irradiation. The tone of the lithographic process is labeled as positive or negative depending on whether the exposed regions are rinsed away (positive tone) or remain (negative tone) when the film is rinsed with the developing solvent. This critical step of converting the chemical “latent image” formed during exposure into a three dimensional relief pattern is referred to as “development”. It is achieved through spray, puddle, or immersion methods. After creating the relief structures, standard processes such as etching, thin film deposition, or ion implantation can be performed in the opened regions. Finally, the resist structures are removed via a liquid stripping process or a dry oxygen plasma etch without altering properties of layers beneath the resist.
Figure 1-2: A schematic illustrating the basic steps of a lithographic process including coating, exposure, development, and post pattern processing such as deposition or stripping.
1.2. Electron Beam Lithography

It has been recognized since the early 1970’s that a finely focused beam of electrons can be accelerated at a resist surface to produce very high resolution patterns since the wavelength of electrons are more than three orders of magnitude smaller than ultraviolet photons. Electrons can be scanned across a resist surface either by systems discretizing a pattern into a series of pixels through sequential exposure or a parallel exposure of all pixels through illumination and projection of a mask onto the wafer plane. In a direct write approach, the electron beam is controlled externally through a computer generated pattern file which directs a tightly focused electron beam to desired locations on the resist surface by deflecting and turning the beam on and off according to the pixilated patterns. The pattern file can contain billions of pixels that have to be dwelled by the electron beam according to a predefined dose. The total write time can be reduced by using higher electron beam currents and high sensitivity resists. Even though significant advancements have been made in optimizing writing strategies, the complexity of the patterning information has steadily increased over the years, which in turn has drastically increased the total number of pixels. Thus, implementation of direct write electron beam lithography in a semiconductor high volume manufacturing environment has been impeded by low throughput processing. Projection electron beam exposure techniques have been developed in analogy to optical projection lithography systems where the path of information flow is directed from a mask onto a wafer plane in order to improve throughput of electron beam lithography systems. In projection electron beam lithography, a mask consisting of a patterned high atomic number scattering layer
on top of a thin “transparent” membrane is utilized. Electrons striking the high atomic layer are backscattered into the electron column while those striking the thin membrane are transmitted to the resist for pattern delineation.

Projection based electron beam lithography is considered as a candidate for next generation lithography in semiconductor manufacturing due to its high resolution and pattern placement capabilities. The paradigm shift to using electron beams for generating patterns in a resist would allow the semiconductor industry to continue on a Moore’s law path of device integration. Utilizing the extremely small wavelength of electrons as a patterning radiation would enable fabrication of semiconductor devices with critical dimensions below 45 nm that is projected for manufacturing starting in 2009\(^6\). The relentless integration of devices through miniaturization could be theoretically continued with electron beam lithography down to size scales of the diameter of a finely focused electron beam which is on the order of about 1 nm\(^7\). Electron beam lithography has been primarily utilized in the semiconductor industry as the standard method for fabrication of critical level masks used in optical lithography. Electron beam writing of high resolution masks is a low volume manufacturing process where throughput is less important and the resolution and registration of patterns are of utmost concern. Direct write electron beam technology will continue to be the highest fidelity and principal method for manufacturing extremely high value and high resolution products such as photomasks due to its superior resolution. Electron beam technology is also steadily progressing into mainstream semiconductor manufacturing with the development of projection electron beam lithography tools. The advent of high throughput electron beam processing tools
could provide the path for the fabrication of next generation semiconductor devices beyond the 65 nm node\textsuperscript{8}.

1.3. Electron Beam Resists

As the incident electrons interact with a solid medium through elastic and inelastic collisional processes, energy is continuously transferred from the traversing electron to the solid target. Energy can be transferred both during the collision and in-between successive collision events. The electrons are decelerated between successive collisions by the solid medium where the stopping power primarily depends on the density of atoms of the target and incident electron energy. Energy can also be transferred during inelastic collisions with atoms in the solid medium through generation of secondary species which in turn can produce other electrons. The energy absorbed by the medium through these electron trajectories generates a latent image that could be developed into relief patterns. Latent image formations in electron beam processes are most commonly realized through chain scission that causes fragmentation of high molecular weight polymers into smaller chains. Therefore, distinction between exposed and unexposed regions is obtained through modifying molecular weight distributions within the patterning film. A chain scission event could also induce crosslinking events by generating radicals within the resist for increasing the molecular weight distribution in the exposed regions for negative tone behavior. Chain scission imaging methods are classical approaches for obtaining latent images in single component resist systems in
electron beam lithography. Another commonly utilized approach in electron beam lithography is a multicomponent scheme where a sensitizer molecule causes dissolution modification in the exposed regions of the polymer matrix. In this approach, the latent image is obtained from energy transfer to the sensitizer molecule causing degradation into its ionic pairs or neutral species that can catalyze reaction events needed for solubility differentiation. Most commonly photoacid (PAG) and photobase (PBG) generators are utilized as sensitizers in resist formulations. The mechanism of latent image formations obtained in organic and inorganic resists during electron beam patterning and some of these conventional resist schemes are described in the following paragraphs.

1.3.1. Organic resists

Electron beam resists consisting of carbon, oxygen, hydrogen, nitrogen, and/or sulfur are classified as organic resists. These resists are typically polymeric materials that can be processed with ease due to their solubility in numerous casting solvents used for deposition. The most prevalent resist polymers in electron beam lithography include acrylates, sulfones, epoxies, and chemically amplified resists. The various electron beam resist polymers are further discussed in the following paragraphs.

The most extensively used electron beam resists are based on acrylates that provide high resolution, ease of handling, wide processing latitude, and excellent film forming characteristics. Poly(methyl methacrylate) (PMMA) has exhibited very high resolution of 3 nm at 200 keV accelerating potential. The electron beam irradiation
induced chain scission mechanism in this system is illustrated in Figure 1-3. The main chain scission event occurs between the main chain carbon and the carbonyl carbon ejecting a methyl formyl radical (CO₂CH₃). This radical further decomposes to form CO₂, CO, CH₃, and CH₃O as volatile products. Finally, through hydrogen abstraction the main chain radical forms a more comparatively stable C=C double bond. Therefore, distinction between exposed and unexposed regions is realized by changing the molecular weight distribution of the polymer.

Figure 1-3: Electron beam degradation mechanism of poly(methyl methacrylate) causing molecular weight reduction through chain scission of the main chain carbon resulting in stable double bonds and volatile species.

Even though acrylates have demonstrated high resolution, structural modification of the polymer backbone requires high electron beam dosage. It has been shown that the
sensitivity of PMMA can be enhanced by copolymerizing PMMA with polymethacrylic acid (PMA) and polymethacrylic anhydride (PMAN)\textsuperscript{10}. It has been found that the sensitivity could be enhanced from 50 to 20 \( \mu \text{C/cm}^2 \) at 20 keV incident electron energy with inclusion of 20 mol\% PMA in PMMA. Also, formation of a terpolymer consisting of PMMA-PMA-PMAN at a molar composition of 70-15-15 has been shown to increase the sensitivity to 10 \( \mu \text{C/cm}^2 \)\textsuperscript{11}. Enhancement in sensitivity with the terpolymer is attributed to higher chain scission efficiency of the different acrylic groups incorporated in the polymer matrix. It has been reported that the gas evolution ratio during electron beam exposures of the terpolymer to be 1:2:6 for PMMA-PMA-PMAN, respectively. The sensitivity of acrylate polymers can also be enhanced by varying the development protocol and developer concentration. Use of an ultrasonic agitation development protocol instead of a standard puddle development protocol has been shown to enhance sensitivity. It has also been found that the sensitivity can be enhanced from \( \sim 7.5 \mu \text{C/cm}^2 \) to \( \sim 6.4 \mu \text{C/cm}^2 \) for a \( \sim 200 \text{ nm thick film exposed at 20 keV using an ultrasonic agitation development protocol} \textsuperscript{12}. The effect of agitating the developer during development produces a dissolution front with higher contrast that can distinguish more clearly between exposed and unexposed regions. Another common method of improving sensitivity has been to optimize the developer concentration. Methylisobutylketeone (MIBK) is typically utilized as the solvent to develop patterns in PMMA. However, a binary solvent combination of MIBK and isopropanol (IPA) or water has been shown to enhance sensitivity. These binary solvent mixtures consist of a strong solvent (MIBK) combined with a moderate non-solvent (IPA or water). It has been found that the
sensitivity can be enhanced by 300 $\mu$C/cm$^2$ and 250 $\mu$C/cm$^2$ for 50 keV exposures of a micron thick film with a 1:3 MIBK:IPA and 1:3 MIBK:water developers, respectively$^{13}$.

Electron beam resists based on polysulfones have also been developed as imaging materials. Polysulfones are alternating copolymers of sulfur dioxide and a small chain olefin. These polymers have been researched since the late 1930’s due to their low material cost$^{14}$. The use of these materials for microelectronics applications only came about after Brown and O’Donnell reported that poly(butene-1-sulfone) degraded with high efficiency when exposed to electron beams. Polysulfone polymers undergo main chain scission at the carbon-sulfur bond during electron beam exposure. The radical formed during exposure rapidly depolymerizes into smaller fragments and evolves volatile species. The imaging mechanism is illustrated in Figure 1-4. The exposure reaction can be monitored using infrared spectroscopy by following the symmetric and asymmetric stretches of the SO$_2$ bond and it has been reported that these peaks disappear at very low exposure doses (~2 $\mu$C/cm$^2$)$^{15}$.

![Figure 1-4: Electron beam degradation mechanism of polysulfones causes rapid depolymerization of the main chain into volatile species of which the primary product is sulfur dioxide.](image-url)
Polysulfones are usually incorporated in a novolac matrix with a solids loading ranging between 10 and 20 wt%. The polysulfone functions both as a dissolution inhibitor and as a sensitizer in the unexposed and exposed regions, respectively. Loading of polysulfone in novolac drastically reduces the dissolution of the polymer matrix by several orders of magnitude in an aqueous base similar to the loading of diazonapthoquinone (DNQ) in the classical DNQ-Novolac optical resist system. However, degradation of the polysulfone in the exposed regions modifies the dissolution behavior of the matrix similar to that of the highly soluble novolac resin for obtaining dissolution contrast required for patterning. The primary advantage of using polysulfone systems is the high sensitivity to electron beam irradiation offered by the rapid depolymerization of the carbon-sulfur bond. The sensitivity of a polysulfone-novolac polymer has been reported to be of the order of $5 \mu$C/cm$^2$ at 10 keV accelerating potential for a 500 nm thick film$^{16}$. 100 nm dense line and space patterns have been demonstrated with a 200 nm thick film at 20 keV accelerating potential$^{15}$.

Another common organic electron beam resist approach has been to utilize epoxies as a polymeric patterning medium. Epoxy based polymers were the first high performing negative tone electron beam resists utilized in the microelectronics industry$^{14}$. Electron beam induced structural transformation of the polymer is based on a ring opening event of the epoxy moiety. A generalized electron beam decomposition mechanism is illustrated in Figure 1-5. An initiating species (I) is generated upon electron beam exposure which can be an anion, anion radical, cation, or cation radical. The initiator reacts with the sterically strained epoxy moiety to cause a ring opening event. The linear epoxy oxygen anion can further react with another epoxy moiety to
promote crosslinking between the two species that can lead to further ring opening events. The chain propagation continues until the oxygen anion is quenched with a radical species. Hence, epoxy based polymers exhibit very high sensitivity as a single radiation induced initiator event can result in numerous cross linking events.

![Chemical reaction diagram]

Figure 1-5: Electron beam degradation mechanism of a generic epoxy system where an initial ring opening event initiates crosslinking of adjacent molecules until quenching by another radical.

There have been primarily three copolymers of epoxy based resists those have been investigated: (1) a copolymer of gycidyl methacrylate and ethyl acrylate (COP) (2) a copolymer of gycidyl ether and novolac (SU-8)\textsuperscript{19}, and (3) a copolymer of novolac and ethyl acrylate (ETPR)\textsuperscript{17}. At 25 keV accelerating potential, a 700 nm thick ETPR film exhibited a sensitivity and contrast of 2 $\mu$C/cm$^2$ and 3.2, respectively. Patterned lines exhibited high line edge roughness and resist swelling. The SU-8 resist is commonly utilized in micro-electromechanical systems (MEMS) fabrication as a negative tone...
optical resist for obtaining high aspect ratio structures greater than 20:1\textsuperscript{18}. In recent years, SU-8 has also been investigated as a high resolution electron beam resist for the fabrication of nanometer sized linear gratings that is an extension of its superior micromachining capabilities. Minimum linewidths of 30 nm with exposure doses of about 100 $\mu$C/cm$^2$ at 40 keV accelerating potential have been obtained using a 150 nm thick SU-8 film\textsuperscript{19}. Even though resolution well below 50 nm with high sensitivity has been demonstrated, epoxy based systems suffer from low contrast as the crosslinking reaction can propagate into undesired regions away from the exposed regions. This undesired crosslinking reaction induced at the edge of feature such as an isolated line results in a slight degradation in resolution.

Throughout its history electron beam lithography has been hampered by low throughput processing due to its serial nature of imaging. A simple method of improving throughput is through the use of highly sensitive resists such as chemically amplified resists that require short dwell times for imaging. Most chemically amplified resists are extensions of the standard poly(hydroxystyrene) polymer blocked with t-butylcarbonyl with a sulfonium acid generator. The imaging mechanism is illustrated in Figure 1-6. In these resists a reactive photoacid generator (PAG) molecule produces an acid upon energy transfer from electrons. After exposure and acid generation, a post exposure thermal bake step is performed to catalyze the reaction between the acid molecule and the protecting group incorporated in the polymer backbone. The deprotection reaction switches the solubility of the polymer in an aqueous base while regenerating the acid that can further “amplify” the reaction within the polymer matrix.
Many different versions of chemically amplified resists exist in the integrated circuit industry with different base polymers, photoacid generators, and dissolution inhibitors as primary components in the polymer matrix. A summary of the important properties exhibited by several chemically amplified resists is listed in Table 1-1. It can be observed that these resists can provide high resolution while requiring low exposure doses. Almost all chemically amplified resists can be imaged well below 100 µC/cm² that provides a major advantage for obtaining high throughput processing. This important property of high sensitivity makes them an ideal candidate as resist platforms.
when projection electron beam lithography tools are delivered for manufacturing. Additionally, a vast amount of research and simulations have been performed in the recent past to understand the dynamics and characteristics of these resist systems that could be utilized for initial implementation of an electron beam lithography process.

Table 1-1: A summary of important lithographic properties of commonly utilized chemically amplified resists in electron beam lithography.

<table>
<thead>
<tr>
<th>Resist</th>
<th>Sensitivity (µC/cm²)</th>
<th>Resolution (nm)</th>
<th>Accelerating voltage (keV)</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAL 605²⁰</td>
<td>1.6</td>
<td>50</td>
<td>20</td>
<td>450</td>
</tr>
<tr>
<td>CAMP²¹</td>
<td>60</td>
<td>250</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>AZ DX-561²²</td>
<td>12</td>
<td>200</td>
<td>30</td>
<td>1000</td>
</tr>
<tr>
<td>AZPN 114²³</td>
<td>1</td>
<td>750</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>ARCH²¹</td>
<td>10</td>
<td>100</td>
<td>50</td>
<td>350</td>
</tr>
<tr>
<td>Poly(p-vinylphenol)</td>
<td>2</td>
<td>200</td>
<td>50</td>
<td>500</td>
</tr>
</tbody>
</table>
1.3.2. *Inorganic resists*

Patterning films consisting of atoms besides carbon, oxygen, hydrogen, nitrogen, and/or sulfur are classified as inorganic resists. Whereas organic resists are predominantly polymeric in nature, inorganic resists are usually monomeric species that undergo a drastic change upon irradiation to a converted form which exhibits vastly different dissolution behavior. Most inorganic resists experience film shrinkage due to the drastic change in material properties as the precursor material is transformed by the electron beam irradiation. Much higher exposure doses are typically required for pattern definition in inorganic systems as compared to organic systems. Inorganic resists typically exhibit very high contrast due to an almost digital difference between exposed and unexposed regions. They exhibit excellent etch resistance properties as a virtue of their inorganic content. Inorganic resists can theoretically provide very high resolution due to their low sensitivity and high contrast since electrons diffusing to wide radial locations in the resist film do not deposit the nominally required energy for dissolution modulation. Energy deposited primarily from the center of the Gaussian electron beam causes structural changes whereby high resolution is obtained. Most inorganic resists are deposited through vacuum deposition methods which are cost ineffective and time consuming. However, some inorganic systems that can be spin coated have also been developed recently for use as high resolution resists. These vacuum deposited and spin coated inorganic resists are further discussed in the following paragraphs.
1.3.2.1. Vacuum deposited resists

A popularly studied vacuum deposited inorganic resist system in the past has been based on amorphous glass materials. Amorphous chalcogenide glasses attracted considerable attention as negative tone electron beam resists in the early 1980’s. Resist films were deposited by vacuum methods including thermal evaporation, sputtering, and electron beam evaporation. Thermal evaporation was performed using chunks of chalcogenide at elevated temperatures above 300°C while holding the chamber pressure in the millitorr range. Typical deposition rates were of the order of 0.1 to 0.3 μm/min. For sputtering depositions, bulk targets were utilized with a moderate sputtering voltage of 1 – 2 keV and power densities of about 200 mW/cm². Similar procedures were followed for electron beam evaporation by using bulk targets of a desired material. As expected, deposition rates using sputtering and electron beam evaporation were slower compared to thermal evaporation and were typically below 10 nm/min. The resist films were annealed in a vacuum or nitrogen atmosphere for about 30 minutes at moderate temperatures of about 150°C following deposition.

Singh was the first to report about a chalcogenide glass resist system based on an Ag₂S/As₂S₃ mixture deposited through thermal evaporation. In this resist scheme, a 70 nm thick As₂S₃ layer was deposited on top of a polyimide layer followed by immersion in an aqueous solution of silver nitrate for 1-2 minutes for growth of an 1 nm thick electron sensitive Ag₂S layer on top of the As₂S₃ film. The silver migrates into the As₂S₃ bottom layer upon electron beam exposure forming exposed regions that are highly resistant to development. A two step development protocol was performed using a standard TMAH
developer for 15 seconds followed by a 120 seconds development in a sodium carbonate solution. At 50 keV incident electron energy, the amorphous glass exhibited a sensitivity and contrast of about 5000 µC/cm² and 5.5, respectively. The developed patterns were transferred through the polyimide layer using an O₂ reactive ion etch with a flow rate of 20 sccm/min at 20 mTorr. With this resist a resolution of about 30 nm was obtained with good edge line roughness and high etch selectivities greater than 30:1 were reported.

An alternative chalcogenide glass investigated in the mid 1980’s was a germanium-selenium (Ge-Se) amorphous resist deposited through sputtering and electron beam evaporation. A sensitizing silver layer of about 10 nm in thickness was formed by immersion in an AgNO₃ solution after deposition of Ge-Se. Similar to the Ag₂S/As₂S₃ chalcogenide glass, electron beam exposure causes diffusion of silver into the Ge-Se in order to increase the chemical etch resistance in a solution. At 25 keV incident electron energy, a 70 nm thick Se-Ge with a 5 nm thick sensitizer layer exhibited a sensitivity and contrast of about 10000 µC/cm² and 5, respectively. The impact of the thickness of the silver sensitizer layer on lithographic patterning was also investigated. An optimal thickness of the silver sensitizer layer between 8 and 10 nm was recommended since the penetration depth of electrons in this high density layer strongly depends on the accelerating voltage. It was also found that pattern fidelity mainly depended upon lateral diffusion of the sensitizer. Even though the gradient for diffusion of the sensitizer is much greater in the vertical direction parallel to the electron beam, radial diffusion causes degradation in resolution and rounded features were frequently observed. Thus, the utilization of this resist scheme was inherently limited by the radial diffusion of the sensitizer and the high electron beam dosage required to initiate imaging reactions.
Metal halides and oxides such as Al₂O₃, AlF₃, and LiF(AlF₃) have also been studied as self developing inorganic electron beam resists\textsuperscript{28,29}. These resist materials volatilize completely under the irradiation of an electron beam. It is well known that fluorine has a high probability to volatilize from electron stimulated desorption. LiF also has a high tendency to desorb while the aluminum in AlF₃ and Al₂O₃ is displaced radially within the resist film. It has been reported that the radial diffusion is on the order of 5 nm with aluminum based resist systems whereby only a 10 nm resolution can be obtained from a theoretically infinitely small diameter electron beam. Interestingly, a low dose electron beam exposure of AlF₃ can result in the formation of thin Al metal lines as the fluorine volatizes rapidly prior to mechanical rearrangement of aluminum. These materials are deposited and immediately exposed to electron beams in order to avoid hydrolysis.

At 100 keV incident electron energy, a 40 nm thick AlF₃ film exhibited a resolution of about 15 nm\textsuperscript{30}. A high image contrast was observed between exposed and unexposed regions as significant loss of the material occurs during exposure. However, volatilization of the resist required an extraordinarily high dose of about 2000000 µC/cm\textsuperscript{2} that can only be obtained using very high electron beam currents. The exposure doses can be considerably reduced by using a dual component resist system of LiF(AlF₃). Minimal aluminum content is used in this resist system in order to reduce the high doses required to cause mechanical rearrangement. This resist system exhibited printing doses of the order of 100’s of mC/cm\textsuperscript{2} for varying film thicknesses from 20 to 65 nm at 100 keV incident electron energy\textsuperscript{31}. Even this sensitivity is exorbitant for practical use as an electron beam resist since printing doses on the order of 100’s of µC/cm\textsuperscript{2} would be highly
desired for patterning. Additionally, these resist systems suffer strongly from outgassing of multiple components that can cause degradation of the electron column. Hence, these resists were primarily investigated to study the diffusion and disintegration of materials upon electron beam irradiation.

Another unique method of patterning inorganic resist films is through electron beam irradiation of molecules those are physically adsorbed on a substrate\textsuperscript{32,33}. The exposure causes transformation in the molecular structure that enhances the adsorption properties on the substrate while the unexposed regions can be simply heated to moderate temperatures for desorption. Thus, selective pattern delineation is achieved through enhancing the physical adsorption of the material that produces image contrast for obtaining negative tone resist patterns. The resist is adsorbed onto the surface by low temperature condensation ($<-20^\circ\text{C}$) at very low pressures of about $10^{-10}$ torr. After deposition, the coated surface is transferred under vacuum for electron beam exposure and brought to room temperature for initiating the desorption reaction. The most successful route demonstrated in electron induced decomposition of adsorbed molecules involves exposure of titanium isopropoxide [Ti(O\text{C}_3\text{H}_7)_4] which is converted to a nonvolatile titanium oxide. A 5Å thin film of titanium isopropoxide has exhibited a sensitivity of about 23 $\mu\text{C/cm}^2$ at 10 keV incident electron energy. Large patterns have been printed using this resist scheme and transferred into a layer beneath using a reactive ion etch. Even though the resist exhibits high sensitivity to electron beams, the process is hindered by requirement of ultra high vacuum tools. Complication in processing from deposition to desorption curtail the process for possible application in special III-V device fabrication.
1.3.2.2. Spin coated resists

The ability to spin coat resist materials eases the lithographic process considerably by eliminating vacuum deposition tools that are time consuming and require high operational cost. The most common inorganic spin coated electron beam resist has been Hydrogen Silsesquioxane (HSQ). HSQ is a spin on glass utilized commonly in the semiconductor industry as a low dielectric constant material. It provides dielectric constants ranging between (2.6-3.0) while exhibiting high thermal stability, good gapfill, global planarization, and crack free adhesion to metals. HSQ is an oligomer composing of a caged silsesquioxane along with a linear Si-O network. A standard thermal cure is performed to convert the caged species to the highly crosslinked network through hydrolysis and condensation of the reactive Si-H functionalities. In 1998, Namatsu found that the curing reaction could also be accomplished through electron beam irradiation. It was proposed that the silicon hydrogen bonds are scissioned during electron beam irradiation and are converted to silanol (Si-OH) groups in the presence of absorbed moisture in the film. These silanol groups are unstable and condense to breakdown the caged molecule into a linear network. This transition drastically decreases the dissolution rate of the matrix in an aqueous base for formation of negative tone resist patterns. Furthermore, HSQ can also be utilized in a bilayer lithography scheme due to its high etch resistance properties where the patterns are transferred through a planarizing layer using a reactive ion etch.

HSQ has demonstrated excellent resolution capabilities at both low and high incident electron energies. A very thin HSQ layer of 20 nm on top of a 180 nm
underlayer has demonstrated resolution on the order of 50 nm at 1, 2 and 3 keV accelerating potential. The exposure doses required to cause the conversion of the caged species to the network form was of the order of about 50 µC/cm². These exposure doses are relatively high considering that chemically amplified resists can be imaged well below 10 µC/cm² at these low incident electron energies. Resolution well below 50 nm has also been demonstrated at higher incident electron energies as well. 20 nm patterns have been fabricated at 50 keV accelerating potential using a 90 nm thick film. Similar to low energy exposures, a high imaging dose on the order of 1400 µC/cm² was required for pattern formations. High aspect ratio patterning has also been demonstrated using incident electron energies of 30 keV with a 50 nm thick film on top of a hard baked novolac layer. Using an O₂ reactive ion etch for pattern transfer, aspect ratios of about 20:1 were obtained with the bilayer lithography process. HSQ has shown great potential as a negative tone electron beam resist by demonstrating extremely high resolution but at a cost of high imaging doses. The contrast between exposed and unexposed regions is much lower than traditional chain scission electron beam resists due to its oligomeric nature.

Inorganic resists provide higher etch resistance properties but exhibit much lower sensitivities as compared to organic resists. An optimal electron beam resist formulation would combine the high sensitivity property of an organic resist with the high etch resistance property of an inorganic resist. In order to achieve such optimal resist performance, many researchers have included nanoparticles to an organic resist in order to increase the etch resistance while retaining high resolution patterning and high sensitivity properties. The distribution of nanoparticles in a polymer film can be
assumed to be homogenous and random at low loadings such that coagulation is not observed. Phase segregation of the nanoparticles from the polymer film typically occurs beyond ten weight percent nanoparticle loading which prohibits the formation of a high quality spin coatable film. The nanoparticles most studied in detail so far have been fullerenes and silica included in a chemically amplified resist matrix. It has been shown that a 7 wt% loading of silica in ZEP520® resulted in a twenty fold reduction in etch rate in an ashing oxygen plasma. A resolution of about 50 nm was demonstrated with the ZEP520®/Silica nanocomposite system while retaining the high sensitivity property of the polymer39. It has been postulated that a nanoparticle loaded resist also enhances the mechanical resistance during wet development that can reduce collapse of the resist features. The loading and distribution of the nanoparticles in the hybrid resist scheme strongly influence the performance of the organic/inorganic matrix. A critical loading level of nanoparticles would be required to affect the lithographic properties of the matrix. High loadings could possibly result in a degradation of resolution and sensitivity of the matrix. The nanocomposite resist approach along with patternable inorganic spin on glass materials are the two of the common spin coatable approaches developed as viable inorganic electron beam resist materials.

1.4. Motivation and Objectives

Electron beam inorganic resists have demonstrated superior potential for high resolution patterning below 20 nm. This ability to pattern high resolution structures
provides unique opportunities in development of nanometer sized semiconductor devices such as single electron transistors and dot structures for quantum computing. A uni-dimensional line written by scanning an electron beam is utilized as a tunneling path between a source and a drain in order to signal a transition between states in a single electron transistor. The one dimensional line represents an island through which electrons can migrate from the source to the drain. The tunneling barrier strength of the island is mainly dependent upon its critical dimension as smaller sizes can provide improved tunneling characteristics for the fabrication of advanced single electron transistors. The fabrication of dot structures for quantum computing also requires patterning of nanometer sized contacts and holes where electron tunneling between dots provides a signal representing a transition between states. Each quantum dot represents an electron in either a spin up or spin down position. Therefore, the spin states of adjacent dots are probed for exchanging information about the state of a logic operation. The performance of a quantum device drastically improves as the size of the quantum dot decreases whereby the tunneling barrier between the dots becomes higher in order to reduce the leakage of electrons between dot structures. The fabrication of high resolution dots and lines is a critical requirement to the realization of these futuristic device structures.

High resolution patterning is also critical in applications such as nanometer sized gratings, critical level masks, and templates for imprint lithography. Fabrication of nanometer sized gratings require minimal defects and low line edge roughness for optimal transmission and distribution of light. Inorganic resists exhibit superior line edge roughness compared to organic resists and are ideal for the fabrication of gratings. The
ability to pattern materials with low line edge roughness provides the capability to pattern high precision masks using inorganic resists. High precision masks for next generation lithography require high pattern placement accuracy and narrow critical dimension control. An extension of high precision mask fabrication is in patterning templates for imprint lithography. In this lithography scheme, a template is pressed onto a resist coated substrate for achieving pattern transfer thereby eliminating issues regarding optics and resists. It has been recently shown that hydrogen silsesquioxane is an ideal candidate as an imprinting material due to its high impact strength and toughness. 30 nm dense line and space patterns have been achieved after pattern transfer to the resist using HSQ as an imprinting medium.

Inorganic electron beam resists require further development and enhancement for supporting these various applications. Most inorganic resists are deposited through vacuum deposition methods which increase fabrication cost and make their use infeasible. Currently the primary inorganic electron beam resist being utilized is hydrogen silsesquioxane due to its ease of processing. Hence, it would be desired to develop inorganic resist materials that can be spin coated to form uniform films required for patterning. In this thesis, a novel method of utilizing radiation sensitive metal-organic precursors is developed and characterized. These precursors can be deposited through traditional spin coating methods to form high quality films and are developed as alternative inorganic resists materials. Besides developing metal-organic precursors, the performance of hydrogen silsesquioxane is enhanced by including a sensitizer for reduced electron beam imaging doses. The sensitizer amplifies the curing reaction occurring in HSQ for reduced exposure times for improved throughput. Furthermore, the
differences between inorganic and organic resists are investigated by developing a
FORTRAN program to perform Monte Carlo simulations of electron trajectories in thin
film materials. The consequences of adding nanoparticles to an organic resist are
explored through a newly developed Monte Carlo approach for a hybrid system. Electron
beam patterning of self assembled monolayers that utilizes backscattered electrons from
high atomic number species substrates is also studied through Monte Carlo simulations.
These studies and investigations are the focal theme of the thesis and are described in
more detail in the following paragraphs.

1.4.1. Development of metal-organic precursors as high resolution electron beam resists

A novel resist imaging scheme utilizing radiation sensitive metal-organic
precursors has been developed recently for optical and electron beam lithography
applications40. In this approach, metal-organic precursors are dissolved in appropriate
casting solvents and deposited onto substrates via traditional spin coating methods. High
optical quality amorphous films with uniform thicknesses are obtained and the casting
solvent is removed through soft baking at moderate temperatures. The metal-organic
precursor is converted to the insoluble metal oxide upon optical or electron beam
irradiation through cleavage of the bulky organic ligands on the precursor. The metal-
organic imaging scheme was originally developed to directly pattern high dielectric
constant metal oxides structures through photolysis for low cost fabrication of integral
capacitors in high density packaging applications. Traditional metal oxide patterning
requires an etch step after blanket deposition which adds numerous fabrication processing
steps and utilization of vacuum tools those are cost ineffective in packaging applications. The high dielectric constant metal oxide can be directly photopatterned in this novel imaging approach while the unexposed regions can be readily removed using common developers.

Metal-organic precursors are also extremely viable as inorganic resists in electron beam lithography. The precursors are soluble in common organic solvents such as methylisobutylketone, xylenes, and hexanes whereby high quality films can be spin coated for ease of deposition and processing. Besides utilizing optical or electron beam irradiation to achieve conversion to the metal oxide, a simple thermal baking step at moderate temperatures (<200°C) could also be performed for blanket conversion. This unique conversion method allows for various processing advantages such as lowering exposure doses for imaging and completing conversion to the metal oxide form after patterning. Lowering of exposure doses can be achieved by performing a dual process with a initial partial conversion thermal baking step followed by electron beam imaging to finish conversion to the insoluble metal oxide form. After exposure and development, the patterns can be fully converted to the metal oxide form for enhancing their etch properties.

As part of this thesis, single and multicomponent metal-organic precursors are developed as viable electron beam resist materials. The development and characterization of titanium metal-organic precursors as high resolution inorganic electron beam resists is described in Chapter 2. Important lithographic properties such as sensitivity, contrast, etch resistance, and hydrolytic stability is studied. The consequences of adding high atomic species precursors based on barium and strontium
metal centers is investigated in Chapter 3. Also, in this chapter, a multicomponent system based on barium, strontium, and titanium metal-organic precursors is developed and characterized for the use in electron beam lithography.

1.4.2. Enhancement of electron beam imaging characteristics of hydrogen silsesquioxane (HSQ)

Hydrogen silsesquioxane has been the primary inorganic resist system utilized in electron beam lithography for the past half decade. It has exhibited resolution below 20 nm with a single layer lithography process and aspect ratios of about 30:1 in a bilayer lithography scheme utilizing hard baked novolac as the underlayer. It provides ease of deposition through spin coating for formation of high quality uniform films required for patterning. The polymer matrix can also be simply converted to its SiO₂ form through thermal baking which could be utilized to form very high etch resistance patterns. However, a major drawback with processing HSQ is the high electron beam dose required to cause breakdown of the caged silsesquioxane molecule. The conversion of the Si-H functionalities to the insoluble Si-O-Si siloxane network is a fairly insensitive electron beam process requiring exposure doses greater than 1000 µC/cm² at 100 keV incident electron energy. These printing doses are an order of magnitude higher than those of chemically amplified resists and it would be highly desired to reduce the imaging doses in order to expedite the electron beam process and improve throughput.

One approach to maintaining the desirable characteristics of the HSQ system while lowering the exposure dose required to pattern the material is to develop a method
for “chemically amplifying” the electron beam exposure in a manner similar to that utilized in organic chemically amplified photoresists. In other words, if a sensitizer can be identified that could serve as an electron beam activated or deactivated catalyst for further reaction of the HSQ matrix, then the exposure doses required for such a system may be substantially reduced. The exposure and decomposition of the sensitizer should either result in the formation or destruction of a catalytic species that can participate as an intermediary for the curing reaction. This kind of amplification mechanism has been known to occur in silicone chemistry where the Si-H functionalities can be rapidly converted to silanols (Si-OH) in the presence of a base catalyst and absorbed moisture within the film.

As part of this thesis, both photobase generators and photodecomposable bases are investigated as sensitizers for amplifying the curing reaction in Chapter 4. The consequences of adding the sensitizers on lithographic performance are evaluated by measuring sensitivity and contrast along with the enhancement in imaging doses for high resolution single pixel wide electron beam exposures. Changes in sensitivity and contrast are monitored for various post exposure bake temperatures used to thermally catalyze the amplification reaction. It is also found that the addition of sensitizers can affect the intrinsic undesired hydrolysis reaction which occurs in HSQ when stored in solution. It is shown that appropriate selection of a sensitizer that drastically changes nucleophilicity before and after exposure is well suited for enhancing the imaging properties of hydrogen silsesquioxane.
1.4.3. Characterization of inorganic resist performance using Monte Carlo simulations

The interaction between impinging electrons and an organic or inorganic resist mainly differ due the high atomic number species atoms contained in inorganic systems. While organic systems contain low atomic number species such as carbon, oxygen, and sulfur, inorganic systems include higher atomic species such as silicon and titanium. Inclusion of these high atomic number species improves etch performance and can provide a higher dissolution contrast between exposed and unexposed regions for obtaining high resolution. Differences between organic and inorganic resists can be studied using Monte Carlo methods which simulate electron trajectories through a solid medium. In this method, scattering characteristics such as scattering angle and energy losses are simulated using random numbers through certain formulas describing the scattering processes. Finally, a large number of these electron trajectories are simulated to obtain good statistical averages for the material behavior and to extract information about the electron-solid interaction.

As part of this thesis, Monte Carlo simulations are employed to study the implications of high atomic number species in electron beam lithography. The effects of adding high atomic number species such as silicon and titanium in a resist is compared to a standard organic resist in Chapter 5. Also, in this chapter, the hybrid Monte Carlo approach used to investigate the influence of nanoparticles in an organic resist is described. The effects of high atomic number species are solely isolated by investigating a polymer molecule tagged with either a silicon or a titanium atom. Electron trajectories of various incident energies are simulated to find the range where optimal performance of
inorganic resists is obtained and compared with organic resists. The inclusion of nanoparticles in an organic resist is also simulated by developing a hybrid Monte Carlo method assuming a standard linear mixing rule at low loadings for the properties of the matrix. The assumption was verified by using a site percolation model to study the changes in material properties away from a reference location to determine a critical threshold distance required to assume isotropy in material properties. Therefore, simulations were performed for cases where the mean free paths of the fast electron trajectories were much greater than the threshold distance where a linear mixing rule is valid for material property estimation. A PMMA polymer loaded with silica (SiO₂) nanoparticles was simulated for the investigation. The lithographic performance of the nanocomposite system was characterized for loadings ranging from 0 to 10 wt% for various incident electron energies.

Furthermore, the consequences of electron beam lithographic patterning of self assembled monolayers that utilize backscattered electrons from the silicon substrate are also investigated in Chapter 6. An ultrathin PMMA film on top of a silicon substrate is used to model and simulate the patterning of self assembled monolayers. The energy transfer causing transformation of the monolayer can be provided through forward scattering electrons or from backscattered electrons from silicon substrate. Energy deposition from the different mechanisms is monitored for various incident electron energies and a digital development function is used to quantify the lithographic performance of the self assembled monolayer approach.
CHAPTER 2

2. DEVELOPMENT OF SINGLE COMPONENT METAL-ORGANIC PRECURSORS FOR HIGH RESOLUTION ELECTRON BEAM LITHOGRAPHY

2.1. Introduction

Electron beam resists have traditionally been polymeric materials functioning on the premise of changes in molecular weight distributions brought about through fragmentation of polymer chains exposed to energetic electrons\(^{41,42,43}\). A reduction of the molecular weight in the exposed regions can provide the imaging contrast required for the delineation of positive tone patterns. The generation of radical species during exposure could also be used to induce rapid crosslinking in the polymer matrix resulting in higher molecular weight species in the exposed regions for negative tone patterning\(^{44}\). Another approach to bring about solubility changes is through transfer of incident electron energy to a photoacid generator (PAG) contained within a chemically amplified resist which catalyzes reactions with the polymer backbone to modulate dissolution behavior and provide image contrast\(^{45}\). All of these aforementioned approaches utilize organic polymers with low atomic number species such as carbon, oxygen, and hydrogen. The polymeric nature of organic resists typically results in low to moderate contrast behavior since the unexposed regions could be potentially induced to react by active
species in the exposed regions. The classical epoxy based resist system is a prime example illustrating this undesired characteristic where initiators generated during irradiation could crosslink undesired regions near the edges of exposed pixels. Organic resists also tend to exhibit low etch selectivities during plasma processes due to high hydrogen content that can be readily abstracted by halogen species contained within a plasma to provide highly reactive sites for etching. Therefore, the polymeric nature of the organic systems results in lower etch selectivities relative to oxides and nitrides. Recently, many groups have been pursuing the use of high atomic number species in electron beam resists in order to obtain higher resolution through improved contrast for enhancement of etch resistance. The monomeric nature of inorganic resists necessitates a drastic change upon irradiation for the formation of patterns whereby high contrast can be obtained between exposed and unexposed regions. A higher resolution process is attainable by improving contrast, as mildly exposed regions far away from the origin of the electron beam are not converted beyond the critical threshold required for pattern delineation. The addition of inorganic species to the resist vastly enhances the etch resistance properties of the matrix as most inorganic species form etch products that exhibit low desorption volatility and are only removed from sputtering processes occurring during plasma etching.

In this chapter, a novel inorganic resist process is reported which uses metal-organic precursors that form an insoluble metal oxide network upon electron beam irradiation. In this approach, organic ligands are cleaved from the metal center to create an unstable molecule that further decomposes to form a metal oxide. Therefore, negative tone patterns can be defined due to the difference in dissolution behavior between the
regions of the original precursor and the exposed metal oxide. The precursor film shrinks during exposure since organic ligands are cleaved to form the insoluble metal oxide network. A high dissolution rate contrast is obtained due to the formation of the vastly different metal oxide network that is insoluble in organic solvents whereas the high organic content precursor is readily dissolved. The formation of the metal oxide inherently provides very high etch resistance as the organic species concentration of the precursor film is drastically reduced. Alternatively, these precursors could also be converted to the metal oxide form through ultraviolet optical irradiation or low temperature thermal baking. The precursors exhibit strong absorption bands in the ultraviolet region that permits optical definition of metal oxide patterns. The precursor film can be conveniently converted to the metal oxide through thermal baking whenever patterning is not desired. Also, the delineated patterns, which need not be fully converted to their metal oxide form for imaging, can be fully converted to the metal oxide through thermal baking or radiation exposure after patterning in order to enhance the etch properties and other characteristics of the metal oxide patterns.

In this study, titanium metal-organic precursors were developed for use as high resolution negative tone inorganic resists in electron beam lithography. Various precursors with different ligands bonded to the titanium metal center were investigated as electron beam irradiation sensitive inorganic materials. The precursors were screened by studying the role of ligands attached to the metal center on achieving hydrolytic stability while maintaining electron beam sensitivity required for patterning. It was generally found that smaller ligands attached to the metal center could be readily hydrolyzed due to reduced steric hindrance which allows water to reach the metal center and cause ligand
hydrolysis. An optimal titanium metal-organic precursor material was selected for further lithographic evaluation after screening a variety of precursors. Standard lithographic properties for the development of a viable inorganic resist system such as sensitivity, contrast, and etch resistance properties were characterized. Finally, the high resolution patterning capability of this imaging scheme in electron beam lithography was demonstrated by generating sub-100 nm features both in a single layer and a bilayer lithography scheme utilizing hard baked novolac as the planarizing layer.

2.2. Metal-organic Precursors

Metal-organic precursors are a class of coordination compounds where a group of carbon atoms in an organic ligand interact through ionic or covalent bonding modes with a transition metal atom center. The number of ligands directly attached to the metal center defines the coordination number of the transition metal atom. Ligands that form a ring in which the metal is included are referred to as chelating while those that occupy a single coordination site are termed non-chelating. The chelating ligand can be bonded to the metal center through unidentate, bidentate, or bridging modes as illustrated in Figure 2-1 for a coordination (IV) atom without a non-chelating ligand. Unidentate and bidentate bonding modes occur when one or none of the coordination sites of the metal center are unoccupied, respectively. The chelating ligand can also be bonded to the metal center through highly attractive forces in a bridging mode as well. The size and nature of these chelating and non-chelating ligands determine the hydrolytic stability of the
precursor. In general, the use of a large ligand sterically hinders the metal center from attack by water, thus helping prevent hydrolysis of the compound$^{50}$. Another simple method of enhancing steric hindrance is to utilize a higher coordination metal center which incorporates a larger ligand cloud surrounding the metal center$^{51}$. The nature of the ligand also plays a critical role in hydrolytic stability. It is commonly known that secondary ligands can be more readily hydrolyzed than primary ligands since secondary ligands are more facile as leaving groups$^{51}$.

Figure 2-1: An illustration of the primary bonding modes between a coordination (IV) metal center and a chelating ligand which can be unidentate, bidentate, or bridging.
Metal-organic precursors containing a metal-oxygen linkage such as metal alkoxides (M(OR)ₙ), metal carboxylates (M(O₂CR)ₙ), and metal β-diketonates M(β-dik)ₙ (β-dik=RCOCHCOR’) provide an obvious route for the deposition of metal oxides. Metal alkoxides are most attractive as starting materials due to their commercial availability and high solubility in numerous solvents that ease processing during synthesis⁵². The high reactivity of the M-OR ligands facilitates preparation of various precursors through ligand exchange reactions. However, these precursors tend to degrade through hydrolysis in the presence of moisture and must be stored in an inert environment. Metal carboxylates are much less soluble than metal alkoxides due to their various bridging and bridging chelating bonding modes that cause formation of insoluble oligomeric species⁵¹. In general, 2-ethylhexanoates are the carboxylates with the smallest number of carbon atoms that could be dissolved in organic solvents for most metal centers. Their solubility can be enhanced by incorporating small quantities of metal alkoxides into the solution mixture⁵⁰. These carboxylate precursors are also much less prone to hydrolysis as compared to metal alkoxides. Metal β-diketonates are highly volatile compounds that are commonly utilized as precursors for chemical vapor deposition (CVD) for late transition metals such as barium and strontium⁵⁰. Typically, acetylacetonates where (R=R’=CH₃) are utilized for solution routes while tetramethylheptanedionates (R=R’=tBu) are the primary choice as precursors for CVD.
2.3. Materials and Methods

The molecular structures of the various titanium metal-organic precursors investigated in this work are illustrated in Figure 2-2 and Figure 2-3. The chelating groups were acetylacetonate, ethylacetylacetonate, or 2-ethylhexanoate while the non-chelating groups were either isopropoxide, n-butoxide, s-butoxide, or phenol. The precursors were dissolved in standard solvents such as methyl isobutyl ketone (MIBK) and xylenes and spin coated using a Cost Effective Equipment (CEE) model 100CB spinner/hotplate onto silicon substrates and soft baked at 90°C for 1 minute. The coated precursor film thicknesses were measured using a Vertical Variable Angle Spectroscopic Ellipsometer (V-VASE) from J.A.Woollam Company, Lincoln, Nebraska. Ellipsometric spectra were collected in the wavelength range of 400 to 1100 nm with a spacing of 10 nm at three different incident angles of 65°, 70°, and 75°. The acquired ψ and Δ polarization data for the film/silicon substrate samples were analyzed using the WVASE32 ellipsometry data analysis software (J.A. Woollam) via a Cauchy layer model without absorption. The resulting precursor films exhibited high optical quality with thickness non-uniformity below 2%.
Figure 2-2: Molecular structure of the titanium\((\text{n-butoxide})_2(2\text{-ethylhexanoate})_2\) metal-organic precursor investigated in this work.

Figure 2-3: Molecular structures of acetylacetonate based titanium metal-organic precursors investigated in this work.
Electron beam exposures were performed using a JOEL 5910 SEM, Tokyo, Ltd. The patterns were designed and written using the Nanometer Pattern Generator System (NPGS) from J.C. Nabity Lithography, Bosman, Montana. The electron beam spot size was measured to be about 10 nm at 30 keV accelerating potential using a gold standard purchased from E.F. Fullam, Latham, N.Y. The electron beam focus was optimized using the gold standard with coarse adjustments beginning at a magnification of 10,000 with continual fine adjustments up to 100,000. Also, small silver dots were placed on the wafer using a toothpick as focusing guides for adjustment and optimization of the electron beam prior to exposure. The beam current was measured using a built-in coupler coated with carbon black paste and the exposures were performed with a beam current of 10 pA. For contrast and sensitivity measurements, a 4 by 4 array of 10 µm square pads were exposed at varying doses and repeated three times on the sample for the purpose of collecting statistical information. After exposure, the films were developed and the step heights of the exposed pads were measured using a Dimension 3100 atomic force microscope with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara). A spin development protocol consisting of a 30 second rinsing step at 250 RPM followed by a drying step for 60 seconds at 1000 RPM was utilized. During the rinse step, fresh developer was poured over the spinning wafer piece using a pipette. Three response curves were obtained for each exposure dose array and the average contrast and sensitivity are reported. Single pixel wide exposures were printed for high resolution patterning with varying doses at a magnification of 1000 and the spin development protocol was used to develop the patterns.
The etch performance of the metal-organic precursors was compared with standard resist polymer backbones such as novolac and polyhydroxystyrene (PHOST) in ashing and oxide etch processes. A Plasma-Therm reactive ion etcher (RIE) 710 was used for etching the different films. The ashing plasma consisted of oxygen (O₂) and argon (Ar) etch gases flowing in a ratio of 40:16 sccm, respectively, at a chamber pressure of 100 mTorr and a power of 200 W. The argon gas was added to increase the anisotropy of the etch process. CHF₃ and O₂ etch gases in a flow rate ratio of 22.5:2.5 sccm were used for the oxide etch process. The chamber pressure was maintained at 70 mTorr and the RF power was 150 W. Thick films were spin coated onto silicon wafer pieces and placed in the etch chamber simultaneously to determine the etching characteristics. The thickness of the films were monitored using ellipsometry at various etch intervals to determine the etch rate and etch selectivity. All ellipsometry data were obtained from 400 to 1100 nm with a spacing of 10 nm at three different angles (65°, 70°, and 75°).

2.4. Results and Discussion

2.4.1. Hydrolytic stability

The hydrolytic stability of the various titanium metal-organic precursors was compared by monitoring changes in film thicknesses as a function of time under standard
laboratory atmospheric conditions (~40-50 relative humidity). Precursor solutions were spin coated onto silicon substrates and soft baked in order to remove excess solvent. An ellipsometric spectrum was collected immediately after spin coating and baking in order to obtain the initial thickness of the precursor film. Afterwards, ellipsometric spectra were collected at regular intervals to monitor the film thickness for up to 72 hours in a relative humidity and temperature of about 40% and 18°C, respectively. Figure 2-4 compares the hydrolytic stability of several acetylacetonate based titanium precursors. It can be observed that increasing the size of the nonchelating ligand improves the hydrolytic stability of the precursor film. The hydrolytic stability improved as the nonchelating ligand was increased in size from isopropoxide, n-butoxide, to phenol. Almost no film thickness loss was observed with the titanium(phenox)2(acetylacetonate)2 precursor. As the nonchelating ligand was changed to a smaller n-butoxide, 25% of the original film thickness was lost during the first 24 hours. Further, the transition to an even smaller isopropoxide ligand reduced the film thickness by about 60% during the first 24 hours. It is well known that the hydrolysis reaction in these precursors proceeds via attack of the metal-ligand bond by airborne water resulting in the formation of a reactive metal-hydroxyl (M-OH) bond52. Two metal-hydroxyl groups can react with each other and condense to form a metal-oxide-metal network (M-O-M). Also, the metal-hydroxyl bond could react with unconverted precursor to induce further network formation. However, increasing the size of the nonchelating ligand attached to the metal reduces the propagation and condensation reactions caused by hydrolysis due to improved steric hindrance. It was also observed that secondary nonchelating ligands were more susceptible to hydrolysis as compared to
primary nonchelating ligands. When the nonchelating ligand was changed from n-butoxide to s-butoxide, 20% more loss in original film thickness was observed after 72 hours. This result is expected since secondary chelating ligands are more facile as leaving groups as compared to primary chelating ligands.

Figure 2-4: Hydrolytic stability of various titanium metal-organic precursors based on acetylacetonate chelating ligands under laboratory conditions of 40% relative humidity and 18°C.
Previously, it was found that the nature of the nonchelating ligand could drastically affect the hydrolytic stability of the acetylacetonate based titanium precursors. In this study, the effects of the chelating group on the hydrolytic stability of the precursor film were also examined. The chelating ligands investigated in this study were based on acetylacetonate, ethylacetylacetonate, and 2-ethylhexanoate. Figure 2-5 compares the hydrolytic stability of the different precursor films with varying chelating groups. It can be observed that changing the chelating ligand from acetylacetonate to ethylacetylacetontne while maintaining the isopropoxide as the nonchelating ligand decreases the hydrolytic stability. It can also be seen that the 2-ethylhexanoate precursor is much more stable than the acetylacetonate precursors. After 72 hours, the 2-ethylhexanoate and acetylacetonate precursors containing the n-butoxide ligand lost about 8% and 30% of their initial film thickness, respectively. That is, carboxylate based precursors are much less prone to hydrolyze as compared to the acetylacetonate based precursors. From these hydrolytic stability studies, the titanium(n-butoxide)_{2}(2-ethylhexanoate)_{2} and the titanium(phenoxy)_{2}(acetylacetonate)_{2} were the only precursors that were deemed to be suitable for further lithographic evaluation.
Figure 2-5: Hydrolytic stability of various titanium metal-organic precursors based on 2-ethylhexanoate, acetylacetonate, and ethylacetylacetonate chelating ligands under laboratory conditions of 40% relative humidity and 18°C.

2.4.2. Electron beam degradation

Electron beam irradiation of the metal-organic precursor causes cleavage of the organic ligands to form the insoluble metal oxide network. A ligand cleavage event results in an unstable titanium molecule with an unsatisfied coordination number that induces further decomposition to form a stable metal oxide. During the exposure process, the cleaved and decomposed ligands are released from the precursor film, which
causes film shrinkage. In the selected titanium metal-organic precursor, the chelating and non-chelating groups were 2-ethylhexanoate and n-butoxide, respectively. As mentioned previously, the chelating ligands can be attached to the titanium metal center in various bonding configurations including unidentate, bidentate, and bridging modes. The non-chelating group is bound directly to the metal center without flexibility for different bonding modes. The various carbonyl bonding modes associated with this precursor exhibit typical stretching frequencies between 1400 and 1700 cm$^{-1}$ in the infrared region. Infrared spectra of as coated titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ film and a fully converted film are shown in Figure 2-6. Two broad peaks containing multiple stretches centered on 1400 and 1700 cm$^{-1}$ correspond to the various carbonyl stretching modes. The strong peak at 1556 cm$^{-1}$ is attributed to the bidentate and bridging bonding modes of the 2-ethylhexanoate chelating group. The non-chelating n-butoxide group exhibits ν(CO) stretches at about 1090 and 1034 cm$^{-1}$. Finally, the asymmetric and symmetric methyl stretches are centered at about 2870 cm$^{-1}$ and 2960 cm$^{-1}$, respectively. It can be observed that the absorbance of the various peaks become negligible after electron beam exposure at a high dose of 10,000 µC/cm$^2$. Therefore, electron beam patterning can be performed with these novel materials that provide imaging contrast as the precursor is converted to the metal oxide. This drastic change in the material can also provide high dissolution contrast for patterning of high resolution features.
Figure 2-6: Infrared spectra of titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor in the (a) methyl and (b) carbonyl stretching region of 1300 to 1700 cm$^{-1}$ and 2800 to 3100 cm$^{-1}$, respectively, for as coated and exhaustively electron beam exposed films.
The electron beam conversion of the metal-organic precursor was monitored for varying extent of exposures. Figure 2-7 compares the changes in the infrared spectra for exposure doses of 0, 25, 50, 100, 200, and 400 µC/cm² exposed at 10 keV incident electron energy. The film thickness was maintained at about a micron and a 1 by 1mm pad was printed and repeated thrice to obtain an area of 2 by 2mm for the infrared measurement. Also, the imaging dose for this film thickness and incident electron energy is expected to be about 250 µC/cm². It can be observed that the absorbances associated with symmetric and asymmetric methyl stretches decrease with increasing extent of conversion. This would be expected as the organic ligands are cleaved from the precursor to form the metal oxide upon irradiation. Similarly, the absorbances associated with the carbonyl stretches also decrease in intensity. Further, Figure 2-8 plots the normalized conversion of the precursor to the metal oxide for the various doses. Here, conversion was calculated by measuring the peak heights of the symmetric and asymmetric stretches at 2858, 2874, 2931, and 2958 cm⁻¹ and assuming complete disappearance of the peaks for exhaustive exposure. Thus, the normalized conversion for an as coated film will be one and decrease to zero for high electron beam doses. It is assumed that the intensity of the peaks will assume a baseline after exhaustive conversion. It can be observed that the conversion is a first order process and a conversion level of about 25% is required at the imaging dose of 250 µC/cm². With an exposure dose of 400 µC/cm², the conversion level in the precursor film is about 40%.
Figure 2-7: A comparison of infrared spectra in the (a) symmetric and asymmetric stretching and (b) carbonyl stretching region for varying extent of electron beam exposures of 0, 25, 50, 100, 200, and 400 µC/cm².
Figure 2-8: A plot of extent of conversion for varying electron beam exposures calculated by normalizing the sum of the heights of the symmetric and asymmetric methyl stretches.

2.4.3. Electron beam response curve

The electron beam imaging characteristics of the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor is shown in Figure 2-9. A 500 nm thick precursor film was exposed at 10 keV accelerating potential followed by the spin development protocol in MIBK. The lithographic sensitivity and contrast are defined here as the dose required to
produce development of half of the initial film thickness after exposure and contrast as

\( \gamma = \frac{1}{\log(D_{100}/D_0)} \)

where \( D_0 \) and \( D_{100} \) are the doses at 0% and 100% of the normalized remaining thickness after development, respectively. The titanium(n-butoxide)\(_2\)(2-ethylhexanoate)\(_2\) precursor exhibited a sensitivity and contrast of 495 \( \mu \text{C/cm}^2 \) and 4.8, respectively. A dose of approximately 250 \( \mu \text{C/cm}^2 \) was required to cause minimal dissolution contrast while doses greater than 950 \( \mu \text{C/cm}^2 \) resulted in negligible loss of film thickness. During electron beam exposure the precursor film shrinks as organic ligands are cleaved from the precursor to form the metal oxide. At the lithographically useful dose of about 1000 \( \mu \text{C/cm}^2 \), 20% reduction in the original precursor film thickness was observed. The exposure doses required to pattern the precursor material are higher than traditional chain scission electron beam resists that require on the order of 100 \( \mu \text{C/cm}^2 \) for dissolution modification. As compared with chemically amplified resists which can be patterned well below 100 \( \mu \text{C/cm}^2 \), the exposure doses are comparatively very high. However, the exposure doses required to cause dissolution modulation in an inorganic resist are typically on the order of and greater than 1000 \( \mu \text{C/cm}^2 \). For example, the vacuum deposited resists reviewed in Chapter 1 required doses on the order of 5000 \( \mu \text{C/cm}^2 \) and greater for patterning. Even though the required exposure doses are high, the precursor exhibits very high contrast which is necessary for patterning high resolution features. The observed contrast of approximately 5 is much higher than many organic chain scission systems that typically exhibit contrast between 2 and 3. Further, it should be noted that exposure doses greater than 1000 \( \mu \text{C/cm}^2 \) at 10 keV accelerating potential were required to cause minimal dissolution
contrast with the titanium(phenoxyl)$_2$(acetylacetonate)$_2$ precursor. Thus, the precursor was not further evaluated due to its poor electron beam sensitivity.

![Graph showing electron beam exposure curve of a 500 nm thick titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor film exposed at 10 keV accelerating potential.](image)

**Figure 2-9**: Electron beam exposure curve of a 500 nm thick titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor film exposed at 10 keV accelerating potential.

2.4.4. *Enhancement of sensitivity using pre-exposure thermal baking*

A unique aspect of these metal-organic precursors are the different methods through which conversion to the metal oxide can be realized. In the early history of these
metal-organic precursors within our group, the primary focus was to achieve a directly photo-definable high dielectric constant metal oxide material for use in integral capacitors for high density packaging applications. This low cost process termed “Photochemical Metal Oxide Deposition (PMOD)” eliminates numerous processing steps required in patterning metal oxide films deposited through traditional vacuum deposition methods. The titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor utilized in this study exhibits an optical sensitivity of approximately 700 mJ/cm$^2$ with a high contrast of roughly 10 at 248 nm exposure wavelengths. An alternative method of conversion to the metal oxide is through thermal baking at moderate temperatures (<200°C) for relatively short times (<1 hour). The primary disadvantage with this method is that it is a blanket conversion process where selective patterning cannot easily be obtained. Degradation products are also trapped within the film during thermal baking which results in a higher carbon content during conversion as compared to optical or electron beam conversion processes. Therefore, photochemical conversion is preferred for obtaining high dielectric constant films with minimal carbon content.

The major advantage of the various conversion methods is that they could be utilized as a partial conversion step prior to electron beam patterning in order to reduce patterning dosage. This pre-exposure step is a blanket process where the entire film is partially converted to an extent which the film can yet be removed upon development. Therefore, selective patterning can be achieved by extending the conversion of the exposed regions beyond the critical threshold where the patterns cannot be removed upon development. If the partial conversion step were carried out beyond the critical threshold, patterns could not be developed since the unexposed regions cannot be
removed under the action of a developer solution. In this work, the effects of using partial thermal conversion of the precursor to the metal oxide before electron beam patterning for increasing the sensitivity of the material was also investigated. Prior to examining the dual process combining thermal baking and electron beam irradiation, the effects of thermal baking solely were studied. Thermal contrast curves of the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor were generated using a 150°C bake for development times of 10, 30, and 60 seconds in MIBK. The thermal contrast curves are shown in Figure 2-10 and the critical processing parameters are listed in Table 2-1. Almost all the curves show a similar thermal contrast of about 3.5. Thermal baking could be performed up to 4 minutes with 10 seconds development in MIBK beyond which conversion crosses the critical threshold and patterns cannot be developed. As the development time is increased to 30 seconds, blanket thermal conversion times could be extended up to 8 minutes. Further, it is observed that blanket conversion times cannot be extended beyond 8 minutes even for a development time of 60 seconds. The critical thermal conversion threshold depends upon the development and thermal baking times at a fixed temperature. It would also be expected that the critical threshold could be reached faster with increasing thermal bake temperatures assuming an Arrenhius type reaction rate dependence.
Table 2-1: A summary of thermal contrast and maximum extent of thermal baking that could be performed at 150°C for various development times in MIBK for the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor.

<table>
<thead>
<tr>
<th>Development time (Seconds)</th>
<th>Contrast</th>
<th>Maximum extent of thermal baking at 150°C (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.56</td>
<td>4</td>
</tr>
<tr>
<td>30</td>
<td>3.49</td>
<td>8</td>
</tr>
<tr>
<td>60</td>
<td>3.53</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 2-10: Thermal contrast curves of titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor at 150°C for three different development times of 10, 30, and 60 seconds.
In this work, the enhancement of sensitivity through a pre-exposure thermal bake at 150°C for 1, 2, and 3 minutes with a development time of 10 seconds was investigated. Figure 2-11 shows the response curves for the various combined processes using thermal conversion followed by electron beam exposure. Here, the sensitivity has been defined as the dose required to cause development of half of the film thickness in the allotted development time and the contrast has been defined as the slope of the linear fit between 0% and 100% of the normalized thickness. As expected, the sensitivity increases with longer pre-exposure bake times due to a higher extent of conversion to the metal oxide prior to exposure. The sensitivity and contrast values for the various processes are listed in Table 2-2. As previously noted, the sensitivity and contrast exhibited by the titanium(n-butoxide)_{2}(2-ethylhexanoate)_{2} precursor from electron beam irradiation is about 495 µC/cm² and 4.8, respectively. By using a partial thermal conversion for 1 min at 150°C, the sensitivity was enhanced to 200 µC/cm² while the contrast slightly deteriorates to 4.40. A twofold increase in sensitivity from 200 to 90 µC/cm² was achieved with an increase in thermal bake time from 1 to 2 minutes. However, the contrast of the dual process decreases considerably from 4.40 to 2.34. Minimal enhancement in sensitivity was observed with a further decrease in contrast for thermal baking of 3 minutes.
Table 2-2: A summary of sensitivity and contrast values found for dual conversion processes incorporating thermal bake times of 0, 1, 2, and 3 minutes at 150°C prior to electron beam exposure.

<table>
<thead>
<tr>
<th>Thermal baking time at 150°C(min)</th>
<th>Sensitivity (µC/cm²)</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>495</td>
<td>4.80</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>4.40</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>2.34</td>
</tr>
<tr>
<td>3</td>
<td>73</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Figure 2-11: Enhancement of sensitivity through pre-exposure thermal bakes at 150°C for 60 seconds (circles), 120 seconds (triangles), and 180 seconds (squares).
Thermal baking of the precursor films prior to electron beam exposure effectively reduces the possible chemical contrast between the unexposed and exposed regions of the film since it increases the extent of conversion in the unexposed regions. The maximum contrast as measured by extent of conversion to the oxide form between exposed and unexposed regions of a film is obviously achieved with a process solely based on electron beam exposure. Inclusion of a thermal bake step prior to electron beam exposure reduces the difference that is possible in terms of extent of conversion between the exposed and unexposed regions. The difference in extent of conversion decreases with increasing thermal bake time prior to exposure as lower electron beam doses are required to render the film insoluble in a developer. Therefore, the overall contrast of the process decreases as a consequence of this lower difference in the extent of conversion between patterned and unpatterned regions. That is, to a first approximation contrast can be thought of as proportional to the ratio of dissolution rate between unexposed and exposed regions. A high ratio would be desired for a negative tone resist system since the unexposed regions are readily washed away as compared to the exposed regions. However, the dissolution rate of the unexposed regions nears that of the exposed regions with increasing thermal bake time prior to exposure. Hence, the dissolution contrast between the patterned and unpatterned regions are reduced during the development process which results in an overall reduction of the contrast.
2.4.5. *Precursor etch studies*

The etching behavior of the titanium metal-organic precursor was studied in both ashing and silicon dioxide etching plasmas. The plasma etch resistance of the films was found to depend strongly upon the extent of conversion of the precursor to the metal oxide network. The organic content of the precursor film decreases upon conversion to the metal oxide, thus altering the etch characteristics of the film. In this study, two different extents of conversion of the precursor film were studied in the ashing plasma: (1) As coated and (2) As coated and thermally converted at 150°C for 30 minutes. It can be assumed that the precursor film is mostly converted to the metal oxide with the thermal treatment at 150°C and thermal treatments for longer times or higher temperatures will only aid in further densification of the precursor film. Figure 2-12 compares the performance of the fully converted and unconverted precursor films to hard baked novolac (2 hours at 180°C). The etch rates for the hard baked novolac, unconverted precursor, and thermally converted precursor in the O₂/Ar plasma are 285.72, 71.64, and 2.37 nm/min, respectively. The unconverted precursor looses thickness during the initial stages of the etch process as the organic ligands are etched away while the titanium atom begins to form a metal oxide capping layer since its volatility in the oxygen plasma is extremely low. The etch rate reported here is for the removal of the precursor film prior to the metal oxide capping layer formation. In contrast, the fully converted precursor which is mostly in the metal oxide form, hardly losses any appreciable thickness for the duration of the etch process. It is known that thermal conversion leaves behind higher carbon content at the top surface of the film.
which causes the slight decrease in thickness during the first 30 seconds of the etch. However, negligible thickness loss was observed beyond 30 seconds of etching. The etch selectivities of the unconverted and fully converted precursor as compared to hard baked novolac are about 30:1 and 120:1, respectively. The etch selectivity for the fully converted precursor is extremely high as the metal oxide contains minimal organic content within the film that drastically reduces the reaction with oxygen radical species contained in the plasma.

Figure 2-12: An etch rate comparison between titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor and hard baked novolac in an ashing plasma.
The etching performance of the titanium metal-organic precursor was also evaluated in a silicon dioxide CHF₃/O₂ etching plasma. Silicon dioxide etching processes are most common in semiconductor manufacturing since it is utilized as the primary isolation material for separating metal lines. The etching behavior was studied with varying extents of conversion of the precursor: (1) As coated and (2) As coated and thermal converted at 150°C for 30 minutes. Figure 2-13 compares the etch rates of the different precursor films along with novolac and polyhydroxystyrene (PHOST) which are common polymeric resins used in photoresists. The etch rates for the unconverted precursor, PHOST, novolac, SiO₂, and TiOₓ were 74.11, 67.67, 58.33, 17.21, 11.74 nm/min, respectively. Again, it is assumed that the thermally converted precursor at 150°C is fully converted to the metal oxide. Thus, it can be seen that the etch rate of the titanium metal-organic precursor can vary from 74.11 to 11.74 nm/min depending upon the extent of conversion to the metal oxide. The etch rate is reduced by a factor of about 7 when complete conversion of the precursor is achieved. It is also be observed that the etch rate of the fully converted precursor is slightly less than that of the silicon dioxide. The slower etch rate is primarily due to the lower volatility of fluorinated etch products formed during the etching of titanium as compared to silicon. The selectivity between the fully converted precursor film and silicon dioxide is about 1.5:1. However, the etch selectivity between the unconverted precursor, novolac, and PHOST as compared to silicon dioxide ranges from .2:1 to about .3:1. That is, the high organic content films are etched at a much faster rate by the fluorinated plasma as compared to silicon dioxide. Therefore, the etch selectivity between the titanium metal-organic precursor and silicon
dioxide is optimal for a fully converted precursor film which exhibits a smaller etch rate than silicon dioxide.

![Etch rate comparisons between PHOST, novolac, SiO₂, and titanium(n-butoxide)₂(2-ethylhexanoate)₂ precursor film in an CHF₃/O₂ plasma.](image)

**Figure 2-13:** Etch rate comparisons between PHOST, novolac, SiO₂, and titanium(n-butoxide)₂(2-ethylhexanoate)₂ precursor film in an CHF₃/O₂ plasma.

2.4.6. *Electron beam patterning: single layer imaging*

The ability to directly pattern titanium dioxide films has applications in a variety of technologies including solar cells⁵³ and optical waveguides⁵⁴. The titanium metal-
organic precursor used in this work provides a unique approach for obtaining patterned titanium dioxide structures. Multiple pass, single line electron beam exposures using a 20 nm pixel-to-pixel spacing were performed at an accelerating potential of 25 keV. A 180 nm thick titanium precursor film was coated and exposed on a silicon substrate and developed with the spin development protocol discussed previously using MIBK. Figure 2-14 shows a top down view of 70 nm isolated lines printed at 1500 µC/cm². The linewidths of the isolated patterns slightly increases with higher electron beam dosage. The negative tone images exhibit high pattern fidelity with low line edge roughness. The features also exhibit highly uniform linewidths for patterning of critical dimensions. This demonstration of high resolution patterning establishes the novel imaging concept as a new inorganic resist system in electron beam lithography. Metal oxides can be patterned on the nanometer scales for the various application previously mentioned with this unique approach. The metal-organic precursor would be partially converted just beyond the critical threshold at the lithographically useful doses with electron beam conversion. However, using photolysis or thermal baking, the patterns can be fully converted to the metal oxide network form for the desired purpose.
Figure 2-14: Sub-100 nm single layer patterns produced on a silicon substrate by electron beam lithography using a 180 nm thick titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor film.

The patterns can be fully converted to the titanium dioxide through optical irradiation or high temperature thermal baking after electron beam patterning and development. During this conversion process, the patterns will shrink as organic ligands are removed from the structures to form the metal oxide network. This post patterning processing step can drastically enhance the etch resistance properties of the patterns as evidenced in the plasma etch studies of the precursor. In order to investigate the film shrinkage occurring during thermal baking, atomic force microscopy (AFM) was used for scanning the patterns before and after thermal baking. A large 500 nm pattern array was exposed at 1000 $\mu$C/cm$^2$, developed in MIBK for 30 seconds, and scanned before and after thermal baking at 180°C for 15 minutes. The AFM images of the resulting
structures are shown in Figure 2-15. It can be observed that thermal baking of the imaged pattern results in vertical shrinkage with minimal lateral shrinkage. For the electron beam exposure and thermal treatment performed in this study, it was found the patterns shrunk vertically by about 35 nm. The shrinkage is primarily dependent upon the extent of conversion achieved through electron beam irradiation. A high electron beam dose might convert the precursor to an extent which results in minimal vertical shrinkage during thermal baking. However, patterns that have been exposed just beyond the nominally required dose could exhibit high shrinkage due to a lower extent of conversion to the metal oxide.

![AFM cross-section profiles](image)

**Figure 2-15:** AFM cross-section profiles of a 500 nm line-space array imaged in the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor using a dose of 1000 µC/cm$^2$ before and after post-development baking at 180°C for 15 minutes.
2.4.7. Electron beam patterning: bilayer imaging

Bilayer lithography was performed using hard baked novolac as the planarizing layer. A 110 nm thick titanium precursor film was spin coated on top of a 430 nm thick hard baked novolac layer. After exposure and spin development in MIBK, the etch mask was thermally baked at 180°C for 30 minutes to ensure full conversion to the metal oxide. Finally, the metal oxide pattern was transferred through the hard baked novolac layer using an O₂ reactive ion etch. It should be noted that during this work, the inclusion of Argon in the etch gas mixture, which would normally be used to improve the anisotropic nature of the plasma, was found to damage the etch mask and result in redeposition of metal oxide debris. The etch rate of the hard baked novolac in the oxygen plasma was 5 nm/min and a 5% overetch was performed. The etch selectivity of the thermally converted sample for 30 minutes at 180°C as compared to hard baked novolac was greater than 100:1. Figure 2-16 shows a tilted SEM image of the isolated bilayer patterns printed using 1800 µC/cm². The linewidths of the features are about 100 nm with an aspect ratio of approximately 5. These bilayer patterns exhibit much less fidelity as compared with patterns obtained from the single layer approach. The patterns exhibit snake-like images commonly observed in negative tone systems that swell during development and deform due to stress build-up. As the patterns expand in the vertical direction during development, and since the patterns are adhered to the plane of the substrate, the stress is relieved through the formation of sinusoidal patterns. The stress build up in the metal oxide film could have occurred during the post patterning thermal baking which could possibly cause the formation of these sinusoidal patterns which are
then transferred through the hard baked novolac planarizing layer. The residual stress build up in the film during post patterning conversion could be reduced by decreasing the thermal baking temperature. It should also be noted that a slight decrease in the imaging layer thickness is expected due to the trapping of organic species during thermal baking that was noted in the plasma etching study.

Figure 2-16: Bilayer structures produced by imaging a titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ film on a hard baked novolac planarizing layer and pattern transferring the structure using an oxygen plasma.
The formation of the wavelike images was systematically studied for varying post patterning thermal treatments followed by O₂ pattern transfer. The thermal treatment involved baking the electron beam patterned films for 0, 2, 4, 8, and 20 minutes at 150°C. Figure 2-17 compares the top down SEM images of the different post patterned treatment films after pattern transfer for three different exposure arrays. Each row and column of SEM images represents a different post patterning thermal treatment and exposure dose array, respectively. Each row from top to bottom corresponds to 0, 2, 4, 8, and 20 minutes of thermal baking at 150°C. Each column from left to right corresponds to exposure arrays ranging from 1000 to 1500, 1750 to 2250, and 2500 to 3000μC/cm² with a step of 250 µC/cm². It can be observed that redeposition persists during pattern transfer in the patterns for low exposure doses and short thermal baking times below 4 minutes. However, longer post patterning baking treatments for 8 and 20 minutes at 150°C drastically reduce redeposition. It can also be observed that increasing electron beam conversion also results in lowered redeposition. As expected, the longest thermal conversion for 20 minutes results in wavelike image profiles due to the high level of stress built up within the pattern. However, a optimal level of thermal conversion of about 8 minutes at 150°C produces the best patterned structures. This study demonstrates that post patterning treatment is a requirement for bilayer processing of these metal-organic precursors. However, a critical extent of conversion exists for eliminating redeposition while maintaining integrity of the structures.
Figure 2-17: Top down SEM images of pattern transferred bilayer structures with different thermal treatments and exposure arrays. Each row corresponds to a post patterning thermal treatment of 0, 2, 4, 8, and 20 minutes at 150°C from top to bottom. Each column corresponds to an exposure array of 1000 to 1500, 1750 to 2250, and 2500 to 3000 μC/cm².
2.5. Summary and Conclusions

In this chapter, several titanium metal-organic precursors based on acetylacetonate and 2-ethylhexanoates were screened and investigated for use as electron beam irradiation sensitive materials. Most of the alkoxide precursors exhibited poor stability as the metal-ligand bond was readily hydrolyzed. Subsequently, the loss of organic ligands resulted in film shrinkage and loss of electron beam sensitivity and the inability to produce patterned structures. It was found that increasing the non-chelating ligand size improved the hydrolytic stability of the precursor film due to increased steric hindrance of the metal-ligand bond from attack by the water. Primarily, the 2-ethylhexanoate chelating ligand was found to be much more stable than the acetylacetonate chelating group. Further investigation of the titanium(n-butoxide)₂(2-ethylhexanoate)₂ precursor showed moderate sensitivity that could be enhanced using pre-exposure thermal treatments. The unique dual process concept was demonstrated using thermal baking at 150°C for up to 3 minutes prior to electron beam exposure. However, blanket partial conversion prior to patterning required for lowering exposures doses reduces the overall contrast of the precursor film. It was found that the contrast reduced from 4.4 to 2.13 as the extent of partial conversion of the precursor film was increased from 1 to 3 minutes at 150°C. It was also observed that the etch properties of the precursor varies with the extent of formation of the metal oxide. The etch studies were performed in ashing and oxide plasmas covering the entire range of conversion by studying an as coated film and a fully converted precursor film. The etch performance was compared with standard materials such as novolac, PHOST, and silicon dioxide. The
fully converted precursor film exhibited etch selectivities of about 120:1 and 1.5:1 when compared to novolac and silicon dioxide in O\textsubscript{2}/Ar and CHF\textsubscript{3}/O\textsubscript{2} plasmas, respectively. This ability to thermal convert the metal-organic precursors to the metal oxide could be utilized to enhance the etch properties of the patterned films.

The novel metal-organic imaging approach was further demonstrated by patterning sub-100 nm features in both single and a bilayer lithography schemes. In the single layer scheme, a 180 nm thick film was patterned on top of a silicon substrate at 25 keV incident electron energy. Exposure doses on the order of 1500 \( \mu \)C/cm\(^2\) were required to pattern 70 nm features. The patterns exhibited excellent uniformity and low line edge roughness. The relatively high exposure doses could be reduced using a pre-exposure thermal treatment that would lower the contrast of the imaging layer. The bilayer lithography scheme was demonstrated using hard baked novolac as the planarizing layer. Aspect ratios of 5:1 were obtained with this bilayer approach but the patterns were found to be sinusoidal due to the stress buildup in the patterns due to post patterning thermal treatments. Also, addition of argon for enhancing the anisotropy of the etch process was found to damage the metal oxide etch mask and cause redeposition.

Mainly, a novel imaging scheme utilizing metal-organic precursors for directly patterning metal oxides has been developed as a new inorganic resist scheme in electron beam lithography and its utility has been demonstrated by patterning sub-100nm features. Electron beam irradiation causes cleavage of the organic ligands from the precursor which results in the formation of an insoluble metal oxide network. The metal-organic precursors provide facile processing as they are soluble in numerous casting solvents and could be readily spin coated to form high quality uniform films required for patterning.
The metal-organic precursors could also be imaged with DUV optical irradiation or thermally blanket converted that allows for processing flexibilities during patterning such as reducing the exposure doses and enhancing the etch properties of the imaging layer. With these numerous advantages, metal-organic precursors present a unique route for patterning metal oxides in the nanometer scale.
A novel imaging concept utilizing metal-organic precursors as high resolution negative tone electron beam resists was previously demonstrated by patterning sub-100 nm features in a titanium based system. A series of titanium precursors were screened and investigated to find an optimal formulation with appropriate lithographic properties as an inorganic electron beam resist. It was found that a carboxylate based titanium precursor exhibited excellent resolution with moderate sensitivity, high contrast, and high etch resistance along with good hydrolytic stability. Even though the titanium precursor system demonstrated high resolution capabilities, the electron beam imaging doses required for pattern formations were much larger than desired for practical lithographic applications. Consequently, this chapter examines various approaches of enhancing lithographic imaging qualities of the novel metal-organic materials through alternative dual and multicomponent precursor extensions containing the titanium system that would presumably maintain the excellent pattern formation property.

The present chapter explores dual and multicomponent precursor systems based on combinations of high atomic number precursors with barium and strontium as metallic
centers along with the formerly established titanium precursor. The high atomic number barium and strontium precursors were chosen due to their commercial availability and are traditionally utilized as materials for deposition of high dielectric constant metal oxides in primarily high density memory applications. Mixtures of barium, strontium, and titanium metal oxides (BST) that are crystalline exhibit very high dielectric constants for use as capacitor dielectrics in memory devices and as gate oxides in traditional semiconductor devices\textsuperscript{55,56}. Much research has been performed with these materials with regards to electrical properties such as dielectric constant, leakage current, and dielectric breakdown strength deposited through various deposition methods including chemical vapor deposition\textsuperscript{57}, laser ablation\textsuperscript{58}, and r.f. sputtering\textsuperscript{59}. These vacuum deposition methods are not preferred for depositing these materials in lithographic imaging where sustaining high throughput processing is of vital importance. However, the barium and strontium precursors provide the advantage of being soluble in organic casting solvents which allows deposition through standard spin coating procedures to form high quality optical films desired in high resolution electron beam patterning. The deposited dual or multicomponent precursor film can be subsequently converted to its metal oxide form through cleavage of its organic ligands in the exposed regions which establishes imaging contrast for the electron beam definition of high resolution patterns.

The high atomic number barium and strontium precursors utilized in this study were also based on metal carboxylates that were previously developed with the titanium based systems. These precursors are compatible amongst each other that aids the formulation of dual and multicomponent mixtures which produce high quality patterning films. The high atomic number precursors could also be imaged optically through
ultraviolet radiation and low temperature thermal baking in similarity to the titanium based precursors. Thus, processing advantages such as dual conversion for enhancing imaging and etch performance could also be achieved with these alternative precursor systems. It would be expected that the inclusion of high atomic number atoms in a precursor film can greatly enhance etching characteristics as compared to the single component titanium precursors due to the poor volatility of etch products involving barium and strontium\textsuperscript{60,61}. Furthermore, since these precursors are similar in molecular nature to the previously investigated carboxylate based titanium precursors, their imaging contrast and high resolution imaging capabilities would also be expected to be comparable. The addition of high atomic number species could also improve electron beam imaging characteristics due to potential synergetic effects amongst precursors in the matrix and higher yields of secondary electrons. It has been previously shown that the high atomic number precursors included in a patterning matrix exhibit vastly different kinetic behavior before and after the conversion of the titanium precursor during optical irradiation\textsuperscript{62}. In a multicomponent mixture containing barium, strontium, and titanium, the barium and strontium precursors exhibited first order decomposition prior to full conversion of the titanium precursor but essentially terminated converting afterwards. Thus, a similar synergistic energy transfer mechanism could decrease the electron beam imaging requirements for patterning dual and multicomponent systems as compared to the single component system. Further, the inclusion of high atomic number atoms in the imaging matrix could enhance electron beam response through higher yields of secondary electrons during the exposure process. High atomic number species are surrounded by a large electronic shell that upon interaction with the incident electrons can emit secondary
electrons that are known to play a critical role in electron beam transformation of resists\textsuperscript{63}. Hence, higher yields of secondary electrons through incorporation of high atomic number atoms in a resist film could decrease the electron beam imaging doses required for patterning the metal-organic precursor based films.

In this chapter, we investigated the electron beam imaging characteristics of multicomponent precursor systems for potential development as novel high resolution inorganic electron beam resist materials. Initially, the hydrolytic stability of the precursor mixtures were verified and it was generally found that even inclusion of an unstable titanium precursor along with stable high atomic number precursors can result in an overall stable patterning matrix. The effect of including high atomic number species on imaging doses was investigated through addition of a barium precursor in various molar fractions to the previously studied titanium carboxylate precursor. Further, the consequences of incorporating a strontium precursor into a multicomponent system along with barium and titanium precursor was also investigated. These studies were intended to probe the postulation that inclusion of high atomic number atoms in a precursor film can aid its imaging characteristics through synergistic effects and higher secondary electron yields. The etch performance of dual and multicomponent precursors were also compared with the single component titanium precursor in standard etch processes such as ashing and oxide plasmas. Finally, the high resolution patterning capability of these dual and multicomponent precursors systems was examined for applications in high resolution electron beam lithography.
3.2. Materials and Methods

Multicomponent metal-organic precursor films were deposited by spin coating and soft baked at low temperatures (90°C) to remove excess casting solvent. The molecular structures of the high atomic number precursors and titanium precursors used in this study are illustrated in Figure 3-1 and Figure 3-2, respectively. Barium(2-ethylhexanoate) and strontium(2-ethylhexanoate) were purchased from Chemat while titanium(isopropoxide)₂(acetylacetonate)₂ (75 wt% solution in isopropanol) was purchased from STREM chemicals. The preparation of the titanium(n-butoxide)₂(2-ethylhexanoate)₂ precursor was noted in the previous chapter. These precursors were dissolved in methylisobutylketone (MIBK) and spin coated to form high optical quality uniform films. Film thicknesses were measured using a J.A. Woollam Co. Variable Angle Spectroscopic Ellipsometer (VASE). Ellipsometric data was collected over the spectral range of 400 to 1100 nm with a spacing of 10 nm for three different incident angles of 65°, 70°, and 75°. Film thicknesses and optical constants were determined assuming a Cauchy layer dispersion model. The choice of the Cauchy model was deemed appropriate since none of the precursor materials display any appreciable absorbances in the wavelength range selected for analysis of thickness and refractive index profiles. Also, film thicknesses of 200 and 500 nm were utilized for high resolution patterning and determination of lithographic imaging properties such as sensitivity and contrast, respectively.
Figure 3-1: Molecular structures of high atomic number species metal-organic precursors investigated for viability as electron beam sensitive inorganic resist materials.

Figure 3-2: Molecular structures of the titanium precursors investigated in dual and multicomponent systems containing the high atomic number precursors.
The electron beam response of the multicomponent metal-organic precursors was evaluated by measuring sensitivity and contrast. An initial film thickness of about 500 nm was coated on a silicon substrate and exposed at 10 keV accelerating potential. Electron beam exposures were performed using both a large area electron beam exposure tool Electron Cure 5900A and a JSM JOEL 5910 SEM, Tokyo, Ltd. The large area exposure tool provides the capability of exposing an area of about a centimeter in diameter. Both of these exposure tools were utilized to measure and quantify the sensitivity and contrast of the dual and multicomponent systems. For imaging characterization with the large area exposure tool, film thicknesses were measured before and after development through ellipsometry to determine the fractional thickness remaining upon development. The samples were developed by immersing and gently agitating the wafer piece in a 50 mL beaker containing the developer solution for 30 seconds. The wafer pieces were then removed from the beaker and briefly rinsed again in the developer solution and finally dried with a nitrogen gun. For imaging characterization with the JEOL 5910 SEM, 10 by 10 µm pads were exposed and developed with the same protocol. The step heights of the features were determined by using a Dimension 3100 atomic force microscope with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara). The exposure dose array was performed and measured thrice for statistical accuracy and the average values were reported.

High resolution patterning was achieved through single pixel wide electron beam exposures performed using the JOEL 5910 SEM. The details of the experiment were described in the materials and methods section of the previous chapter. For the bilayer lithography process, hard baked novolac was used as a planarizing layer on top of a
silicon substrate. The novolac layer was spin coated to a thickness of about 700 nm and hard baked at 180°C for 2 hours to a final thickness of approximately 500 nm. The multicomponent metal-organic precursor solution was spin coated on top of the novolac layer to form the bilayer film stack. After electron beam exposure and development, the etch mask pattern was transferred to the novolac using an oxygen/argon reactive ion etch. The etch process was performed in a PlasmaTherm 710 at a pressure and power of 200 mtorr and 200 Watts, respectively. Oxygen and argon were used as the etch gases with a flow ratio of 40:16 sccm, respectively. Argon was included in the plasma in order to obtain higher anisotropy. The etching behavior of the dual and multicomponent metal-organic precursor films were studied in both ashing and oxide etch plasmas. Both etch studies were performed using a PlasmaTherm reactive ion etcher using a similar protocol that was described in the previous chapter.

3.3. Results and Discussion

3.3.1. Dual and multicomponent precursor stability

A critical requirement in a lithographic process is the hydrolytic stability of the resist film throughout the patterning steps beginning from the coating to the final removal of the delineated features. It was previously noted that most of the titanium based precursors exhibited poor hydrolytic stability which eliminated them from further
consideration and evaluation for development as high resolution inorganic resist systems. It was primarily found that the carboxylate based titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor was much more stable than the metal alkoxide based acetylacetonate titanium precursor systems. The high atomic number barium and strontium precursors utilized in the forthcoming studies were also based on carboxylates. Therefore, these precursors would be expected to be stable systems considering that the carboxylate based titanium precursor exhibited good hydrolytic stability. Furthermore, assuming that the high atomic number precursors are hydrolytically stable, it might be possible to incorporate one of the unstable acetylacetonate based titanium systems into a precursor matrix which provides an overall stable patterning film. That is, the combination of stable and unstable precursors in a dual or multicomponent mixture could stabilize the patterning film. Thus, the hydrolytic stability of both dual and multicomponent systems containing the barium and strontium precursors were investigated while the titanium precursor was adjusted between the acetylacetonate and carboxylate based versions.

It was previously found that the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor was hydrolytically stable by itself and it would be expected that dual and multicomponent precursors consisting of the high atomic number systems that are also based on carboxylates would also be stable towards undesired hydrolysis. Figure 3-3 plots the normalized remaining thicknesses monitored for the dual and multicomponent systems incorporating the titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor for a duration of 72 hours. The evaluated precursor systems consisted of a 1:1 molar mixture of the barium and titanium precursor and a 1:1:1 molar mixture of the barium, strontium,
and titanium precursors, respectively. It can be observed that minimal film thickness is lost during the duration of the experiment with the addition of the barium and strontium precursors and that the hydrolytic stability of the resulting precursor film improves slightly. A minimal amount of film shrinkage is observed from the possible loss of casting solvent that was not removed from the precursor film during the softbake performed at 90°C for 90 seconds. The remainder of the film thickness loss can be attributed to hydrolysis that occurs to a minimal extent in these dual and multicomponent precursor systems.

Figure 3-3: Hydrolytic stability of single, dual, and multicomponent precursors mixtures consisting of barium(2-ethylhexanoate)₂, strontium(2-ethylhexanoate)₂, and titanium(n-butoxide)₂(2-ethylhexanoate)₂.
It was previously noted that the titanium(isopropoxide)$_2$(acetylacetonate)$_2$ precursor could be readily hydrolyzed as the spin coated film lost almost half its original film thickness after 72 hours. In this study, the hydrolytic stability of the dual and multicomponent systems containing the barium and strontium precursors along with the titanium(isopropoxide)$_2$(acetylacetonate)$_2$ precursor were investigated. Figure 3-4 shows the hydrolytic stability of the dual and multicomponent precursors containing the unstable alkoxide based titanium precursor. It can be observed that the addition of the barium and strontium precursors improves the hydrolytic stability of the precursor film. The 1:1 molar mixture of the barium and titanium precursors losses 30% of its original film thickness after 72 hours. However, the addition of the strontium precursor in a 1:1:1 molar mixture of the barium, strontium, and titanium precursors was found to drastically enhance the hydrolytic stability of the mixture even through the acetylacetonate based titanium precursor is unstable by itself. The multicomponent mixture only lost about 13% of its original film thickness during the entire duration of the experiment. Hence, the incorporation of stable precursors in dual and multicomponent systems where the remaining precursor is unstable can provide a precursor film that exhibits good hydrolytic stability. In the multicomponent mixture, the barium and strontium precursors provide the stability in which the unstable titanium precursor can be incorporated. Finally, it should be noted that directly spin coating the barium and strontium precursors by themselves did not provide a high quality spin coated film for hydrolytic stability analysis.
3.3.2. Consequences of high atomic number species in an electron beam resist

The addition of high atomic number atoms to an electron beam resist can alter its imaging characteristics through enhanced generation of secondary electrons during the electron beam exposure process. It is well known that electron beam transformation of resist materials is mainly accomplished through the generation of secondary electrons that possess excitational energies which cause radical generation or breakdown of...
sensitizer molecules into their ionic pairs in order to form latent image profiles\textsuperscript{64}. Secondary electrons are generated as a consequence of inelastic collisions between the incident electrons and the electronic shells surrounding the atoms from the primary electron trajectory through the resist film. The ejected secondary electrons can also traverse through the resist and further knock off electrons in their trajectories to amplify the effect of electron production within the resist. It has been estimated through Monte Carlo simulations that 80\% of the imaging events occurring at 100 keV incident electron energy in a classical acrylate chain scission resist are caused by secondary electrons\textsuperscript{65}. It has also been shown that energy deposition in an acrylate resist at 25 keV incident electron energy primarily occurs through the 1\textsuperscript{st}, 2\textsuperscript{nd}, and 3\textsuperscript{rd} order knock off electrons\textsuperscript{66}. Further, it has been shown by different authors that the ultimate resolution limiting factor in electron beam lithography are the trajectory of fast secondary electrons through the resist\textsuperscript{67,68}. At very high incident electron energies, the primary electrons traverse a nearly straight line path through the resist while secondary electrons generated in their path can traverse in any random direction which restricts the resolution attainable in electron beam lithography. These studies have demonstrated that the secondary electron spread is about equivalent to the primary electron spread at an incident electron energy of about 100 keV. The generation of secondary electrons depends primarily upon the density of the electron cloud surrounding each of the atoms contained in a resist. The most commonly used atoms such as carbon, oxygen, and hydrogen in organic resists have a relatively small electron cloud density. Therefore, incident electrons have a limited probability of interacting with the orbital electrons in a direct electron-electron collision to cause secondary electron generation. However, the use of high atomic number species with
large electron clouds can drastically enhance the generation of secondary electrons within the resist as the incident electrons have a much higher probability of interacting with the electron cloud through a direct electron-electron inelastic collision. Figure 3-5 illustrates the consequences of incorporating high atomic number species in a resist on secondary electron generation through Monte Carlo simulations that are described in detail in Chapter 6. Secondary electrons are counted for trajectories through the hypothetical resist film tagged with the high atomic number atom with a thickness of 500 nm. It can be observed that the number of secondary electrons generated per incident electron is proportional to the effective atomic number of the resist. The organic based acrylate resist exhibits the lowest probability for secondary electron generation. The addition of a high atomic number species such as titanium increases secondary electron generation by a factor of about 2. Further, it can be seen that the addition of a very high atomic species such as barium enhances the secondary electron generation by a factor of five across all incident electron energies. Thus, the addition of high atomic number species in a resist can be utilized to possibly enhance the electron beam imaging characteristics of the patterning film since a large number of secondary electrons are generated within the resist that could be further utilized for imaging events.
3.3.2.1. Effects of high atomic number species in dual component systems

The Monte Carlo simulations provided insight into the consequences of incorporating high atomic number atoms in an electron beam resist. The addition of high atomic number atoms was found to enhance secondary electron generation that could possibly improve the imaging characteristics of systems such as metal-organic precursors. In order to verify the postulate, we investigated the effects of adding a
second metal-organic precursor that contains a higher atomic number metal species on
the sensitivity of the resulting imaging material. In this work, a barium(2-
ethylhexanoate)$_2$ precursor was chosen since it contains the same chelating ligand as the
titanium precursor, which plays the primary role in the decomposition of the precursor to
the metal oxide upon exposure. The impact of addition of the high atomic number metal
species was studied by imaging different molar combinations of the barium and titanium
precursors. It was not possible to image a pure barium(2-ethylhexanoate)$_2$ film since that
precursor could not be coated into a high quality film. Precursor films of 2:1, 1:1, and
1:2 molar ratios of barium to titanium precursor were spin coated to thicknesses of
approximately 500 nm. The contrast curves for the various mixtures exposed at 10 keV
accelerating potential are shown in Figure 3-6 and the lithographic imaging properties are
summarized in Table 3-1. The titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursor by
itself exhibits a sensitivity of 495 $\mu$C/cm$^2$ and a contrast of 4.9. With the addition of
barium(2-ethylhexanoate)$_2$ precursor in a Ba:Ti molar ratio of 1:2, the sensitivity was
enhanced to 237 $\mu$C/cm$^2$ while the contrast increased to 5.2. Next, the 1:1 Ba:Ti molar
mixture exhibited a enhanced sensitivity and contrast of 157 $\mu$C/cm$^2$ and 4.9,
respectively. However, further addition of the barium(2-ethylhexanoate)$_2$ precursor in a
Ba:Ti molar ratio of 2:1 exhibited a similar sensitivity of 157 $\mu$C/cm$^2$ and decreased
contrast of 3.9. Thus, the optimal ratio for the titanium and barium precursors used in
this work was found to be approximately a 1:1 Ba:Ti molar mixture
Table 3-1: A summary of imaging properties of various molar ratio mixtures of the barium(2-ethylhexanoate)$_2$ and titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Sensitivity (µC/cm$^2$)</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba:Ti – 0:1 molar ratio</td>
<td>495</td>
<td>4.8</td>
</tr>
<tr>
<td>Ba:Ti – 1:2 molar ratio</td>
<td>237</td>
<td>5.2</td>
</tr>
<tr>
<td>Ba:Ti – 1:1 molar ratio</td>
<td>157</td>
<td>4.9</td>
</tr>
<tr>
<td>Ba:Ti – 2:1 molar ratio</td>
<td>157</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Figure 3-6: Electron beam imaging curves of the various dual component precursor films composing of the barium(2-ethylhexanoate)$_2$ and titanium(n-butoxide)$_2$(2-ethylhexanoate)$_2$ in different molar ratios.
3.3.2.2. Effects of high atomic number species in multi-component systems

In the previous section, it was found that introducing a high atomic number species such as barium into the precursor matrix resulted in approximately a three fold enhancement in sensitivity while maintaining moderate contrast behavior. In the current section, the effective atomic number of the precursor film is further increased through incorporation of a strontium precursor along with the barium and titanium precursors. The molecular structure of the strontium precursor is analogous to the barium precursor that is based on a metal carboxylate. Further, it should be noted that the titanium precursor used in this multicomponent scheme is an alkoxide based compound that is hydrolytically unstable by itself but in the presence of stable precursors produces a stable patterning film. The response of this multicomponent metal-organic precursor was also characterized by measuring the sensitivity and contrast. Figure 3-7 shows the electron beam imaging contrast curves for the two different molar mixtures of the multicomponent metal-organic precursor exposed at 10 keV accelerating potential using the large area exposure tool described in the materials and methods section of this chapter. The lithographic properties of the imaging curves are summarized in Table 3-2. The 1:1:1 and 1:1:2 molar mixtures of the Ba: Sr: Ti precursors exhibited a sensitivity of about 70 and 56.5 µC/cm², respectively. The transition between the completely dissolved and undissolved regions for both molar mixtures is sharp and the contrast is estimated to be about 8. The imaging doses for the different molar mixtures of the multicomponent systems are almost similar even though the effective atomic number of the precursor film is increased from the 1:1:2 to the 1:1:1 mixture. This result indicates a critical limit exits
for enhancing the sensitivity through secondary electron generation. A similar result was also observed with the various molar mixtures of the barium and titanium precursors where the sensitivity exhibited by the 1:1 and 2:1 Ba:Ti mixtures were almost identical. Primarily, it has been found that the addition of the strontium precursor to a dual component barium-titanium system further enhances the imaging properties of the precursor film. Again, it is postulated that the sensitivity is enhanced through a higher yield of secondary electrons within the patterning film contributed by the addition of a high atomic number atom.

Table 3-2: A summary of imaging properties of two different molar ratios of a multicomponent precursor system composing of the barium(2-ethylhexanoate)$_2$, strontium(2-ethylhexanoate)$_2$, and titanium(isopropoxide)$_2$(acetylacetonate)$_2$ precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Sensitivity (µC/cm$^2$)</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1:1 Ba:Sr:Ti molar ratio</td>
<td>70</td>
<td>8.1</td>
</tr>
<tr>
<td>1:1:2 Ba:Sr:Ti molar ratio</td>
<td>56.5</td>
<td>7.8</td>
</tr>
</tbody>
</table>
Figure 3-7: Electron beam imaging curves of multicomponent precursor system consisting of the barium(2-ethylhexanoate)$_2$, strontium(2-ethylhexanoate)$_2$, and titanium(isoproponoxide)$_2$(acetylacetonate)$_2$ precursors in two different molar ratios.

The electron beam imaging characteristics of the metal-organic imaging approach has been found to strongly depend upon the effective atomic number of the precursor film used for patterning. Here, the effective atomic number of the precursor film is defined as the sum of the atomic numbers of the metals of the precursor matrix. The sensitivity was steadily enhanced as the precursor system increased in effective atomic number from the single component titanium system, to a dual component barium:titanium system, and finally to a multicomponent barium:strontium:titanium system. Figure 3-8 plots the
sensitivity exhibited by the precursor film versus the effective atomic number of the film. It can be observed that the introduction of a high atomic number species atom such as barium can drastically enhance the sensitivity of the resulting precursor film. Also, addition of the strontium precursor in a multicomponent system assisted in further enhancing the sensitivity of the patterning film. However, a critical limit of addition of the high atomic number species to the precursor film was observed for the dual and multicomponent systems beyond which the enhancement of imaging properties were minimal. For dual component Ba:Ti systems, addition of the high atomic barium precursor beyond a 1:1 ratio was found not to impact the sensitivity of the film but decrease its contrast. Similarly, the 1:1:1 and 1:1:2 Ba:Sr:Ti multicomponent systems exhibited analogous imaging properties. Thus, the imaging dose stabilizes beyond a critical point where the further addition of high atomic number atoms results in minimal enhancement in imaging performance. Interestingly, a linear relationship is observed between the sensitivity and the effective atomic number of the precursor film in a semilog plot. This unique relationship provides insight into how the electrons interact with unconventional high atomic number atoms in a resist and establishes the concept of introducing high atomic number species for enhancing imaging performance of any resist for electron beam processing.
3.3.2.3. Effects of dual processing

Even though the sensitivity of the metal-organic imaging approach was enhanced through the addition of high atomic number species into the precursor matrix, it would be desired to reduce the patterning doses even further. An alternative method that could be used to enhance sensitivity is through pre-patterning thermal treatments or blanket photolysis that partially converts the multicomponent metal-organic precursor film to its
insoluble amorphous metal oxide state. Using pre-patternning thermal treatments and/or blanket photolysis, the multicomponent metal-organic precursor can be partially converted to the desired metal oxide network form in order to reduce the dose required for pattern formation. Hence, a two step or a three step process involving a combination of optical irradiation, electron beam irradiation, and thermal baking can be used to convert the metal-organic precursors to the insoluble metal oxide. However, there will be a restriction to the blanket thermal baking and/or photolysis, beyond which, the unexposed regions cannot be developed to delineate the relief patterns. In this section, we investigated pre-patternning thermal treatments as a processing method to enhance the sensitivity of these metal-organic precursors. Here, we studied the consequences of using a 15 and 30 second thermal bake at 150°C prior to electron beam exposure on imaging characteristics. The thermally enhanced imaging curves are shown in Figure 3-9 and the lithographic properties are summarized in Table 3-3. With a 15 second thermal conversion, the sensitivity was enhanced to 56 µC/cm² with a reduced contrast of 6.4. Similarly, a 30 second thermal treatment prior to electron beam exposure enhanced the sensitivity 23.3 µC/cm² but the contrast decreased to 4.2. The blanket partial conversion decreases the extent of conversion between the exposed and unexposed regions that the developer encounters during the development process. In particular, the development rate of a partially converted region is lower as compared to an unexposed region. The contrast can also be defined in terms of a development rate as the ratio of development between unexposed and exposed regions for a negative tone material. Hence, with blanket partial conversion thermal treatments, contrast decreases as a consequence because of the reduced development rate of the partially converted regions.
Table 3-3: A summary of imaging properties of the multicomponent barium(2-ethylhexanoate)$_2$, strontium(2-ethylhexanoate)$_2$, and titanium(isopropanoxide)$_2$(acetylacetonate)$_2$ precursor system processed with thermal treatments prior to electron beam exposure.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Sensitivity ($\mu$C/cm$^2$)</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron beam exposure of 1:1:2 Ba:Sr:Ti precursor</td>
<td>70</td>
<td>8.0</td>
</tr>
<tr>
<td>15 second thermal treatment @ 150°C prior to Electron beam exposure of 1:1:2 Ba:Sr:Ti precursor</td>
<td>56.5</td>
<td>6.4</td>
</tr>
<tr>
<td>30 second thermal treatment @ 150°C prior to electron beam exposure of 1:1:2 Ba:Sr:Ti precursor</td>
<td>23.3</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Figure 3-9: Electron beam imaging curves of the multicomponent barium(2-ethylhexanoate)$_2$, strontium(2-ethylhexanoate)$_2$, and titanium(isopropanoxide)$_2$(acetylacetonate)$_2$ precursor system for various dual process treatments of 0, 15, and 30 seconds of thermal baking at 150°C prior to electron beam exposure.
3.3.3. Enhancement of etch characteristics through incorporation of high atomic number atoms

It has been previously shown that inclusion of high atomic number species in the precursor matrix can greatly enhance its electron beam imaging characteristics. It is also possible that the etch resistance of the precursor films can be improved through the addition of high atomic number atoms due to the difficulty in the formation and desorption of chemical etch products with transition metals such as barium and strontium. In order to compare the etch performance to single component titanium precursors, the etching characteristics of the dual and multicomponent films were also studied in ashing (O₂) and oxide (CHF₃/O₂) plasmas. Dual and multicomponent precursor films of 1:1 Ba:Ti and 1:1:2 Ba:Sr:Ti molar ratios were investigated, respectively. The carboxylate based titanium precursor was utilized in these studies. The etching performance of two different extents of conversion of an as coated precursor film and a thermally converted precursor film (30 minutes, 150°C) were compared with hard baked novolac (2 hours, 180°C) in the ashing plasma. As expected and observed in the previous chapter with single component titanium precursor films, the etch resistance of the dual and multicomponent systems strongly depends on the extent of conversion of the precursor film to its metal oxide form. Figure 3-10 compares the performance of the as coated and thermally converted dual and multicomponent precursor films to hard baked novolac in the O₂ ashing plasma. The etch selectivities amongst the various films are listed in Table 3-4. The thermally converted films that are mostly converted to the metal oxide form exhibit the best etching characteristics and provide etch selectivities of 145:1 and 161:1.
as compared to hard baked novolac for the dual and multicomponent systems, respectively. It should be noted that the etch selectivity between the thermally converted titanium precursor and hard baked novolac was 120:1. Also, the etch selectivity between as coated films and hard baked novolac is approximately equivalent for all precursor films. Thus, the addition of the barium and strontium enhances the etching characteristics of the precursor film but minimal differences are observed between the dual and multicomponent precursor films in the ashing plasma.

Table 3-4: Comparisons of etch selectivities of dual and multicomponent precursor films in an O₂ ashing plasma.

<table>
<thead>
<tr>
<th>Precursor type</th>
<th>Comparison</th>
<th>Etch selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dual component 1:1 Ba:Ti molar mixture</td>
<td>Hard baked novolac / Thermally converted</td>
<td>145:1</td>
</tr>
<tr>
<td></td>
<td>Hard baked novolac / As coated</td>
<td>4.5:1</td>
</tr>
<tr>
<td></td>
<td>As coated / Thermally converted</td>
<td>32.5:1</td>
</tr>
<tr>
<td>Multicomponent 1:1:2 Ba:Sr:Ti molar mixture</td>
<td>Hard baked novolac / Thermally converted</td>
<td>161:1</td>
</tr>
<tr>
<td></td>
<td>Hard baked novolac / As coated</td>
<td>4.3:1</td>
</tr>
<tr>
<td></td>
<td>As coated / Thermally converted</td>
<td>37.7:1</td>
</tr>
</tbody>
</table>
Figure 3-10: Etch rates of dual (top) and multicomponent (bottom) precursors films as compared to hard baked novolac in an ashing O₂ plasma.
The etching characteristics of dual and multicomponent precursor films were also studied in an oxide etching CHF$_3$/O$_2$ plasma. Similar dual and multicomponent precursor films of as coated and thermally converted at 150°C for 30 minutes were prepared and compared with standard resist polymers such as novolac and polyhydroxystyrene (PHOST) and silicon dioxide. Figure 3-11 compares the etch performance of the various films in the oxide etch plasma and Table 3-5 summarizes important etch selectivities amongst the various films. The etch selectivity between the thermally converted 1:1 Ba:Ti dual component and 1:1:2 Ba:Sr:Ti multicomponent precursors and novolac was found to be about 5.8:1 and 6.6:1, respectively. Similar etch selectivities of 6.4:1 and 6.9:1 were observed relative to PHOST for the dual and multicomponent thermally converted precursor films, respectively. Mainly, the thermally converted dual and multicomponent precursor exhibit an etch selectivity of 1.6:1 and 1.7:1, respectively, as compared to silicon dioxide. In the previous chapter, it was found that the single component titanium precursor exhibited an etch selectivity of 1.5:1 as compared to silicon dioxide. Thus, the addition of barium in dual component system improves the etch selectivity in an oxide etching plasma.
Figure 3-11: Etch rates of dual (top) and multicomponent (bottom) precursors films as compared to novolac, PHOST, and silicon dioxide in a CHF$_3$/O$_2$ oxide etching plasma.
Table 3-5: A comparison of etch selectivities of dual and multicomponent precursor films in an oxide etching CHF₃/O₂ plasma.

<table>
<thead>
<tr>
<th>Precursor type</th>
<th>Comparison</th>
<th>Etch selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dual component 1:1 Ba:Ti molar mixture</td>
<td>Novolac / Thermally converted</td>
<td>5.8:1</td>
</tr>
<tr>
<td></td>
<td>PHOST / Thermally converted</td>
<td>6.4:1</td>
</tr>
<tr>
<td></td>
<td>Thermally converted / Silicon dioxide</td>
<td>1.6:1</td>
</tr>
<tr>
<td>Multicomponent 1:1:2 Ba:Sr:Ti molar mixture</td>
<td>Novolac / Thermally converted</td>
<td>6.6:1</td>
</tr>
<tr>
<td></td>
<td>PHOST / Thermally converted</td>
<td>6.9:1</td>
</tr>
<tr>
<td></td>
<td>Thermally converted / Silicon dioxide</td>
<td>1.7:1</td>
</tr>
</tbody>
</table>

3.3.4. Electron beam patterning

The lithographic imaging properties of the metal-organic patterning approach have been considerably improved through the incorporation of high atomic number species in the precursor film. It has also been shown that the etch resistance can be improved with the addition of a high atomic number species such as barium and strontium. The most important lithographic property of concern with the metal-organic imaging approach is the delineation of high resolution features with good critical dimension control. In this section, the patterning of the multicomponent 1:1:2 Ba:Sr:Ti precursor was evaluated as a high resolution imaging approach for electron beam lithography. The alkoxide based titanium precursor was used in these studies. Single
layer imaging performance was investigated using a 200 nm thick multicomponent precursor film on top of silicon substrate. Single pixel wide exposures were performed at 10 keV accelerating potential and developed in MIBK using the spin development protocol for 30 seconds. Figure 3-12 shows top down micrographs of isolated patterns with linewidths on the order of 100 nm. The top picture shows isolated lines patterned from 400 to 500 µC/cm² with a step of 20 µC/cm² while the bottom picture magnifies the isolated line printed at 440 µC/cm². The linewidths of the isolated patterns show minimal change in their critical dimensions for the various patterning doses. The features exhibit minimal line edge roughness with excellent critical dimension control which one desires in a lithographic process. The patterning doses required for imaging the multicomponent precursor system are about a third of that of the titanium precursor imaging for single pixel wide electron beam exposures. This would be expected as the sensitivity was enhanced through the addition of high atomic number atoms in the precursor matrix. With this demonstration of high resolution single layer patterning, the viability of the multicomponent imaging approach has also been established as a novel inorganic material for electron beam lithography.
Figure 3-12: Isolated line patterning in a 200 nm thick multicomponent 1:1:2 Ba:Sr:Ti precursor on top of silicon at 10 keV accelerating potential with exposure doses ranging from 400 to 500 µC/cm$^2$ with a step of 20 µC/cm$^2$ (top) and a magnified image of the isolated pattern printed at 440 µC/cm$^2$ (bottom).

The imaging aspects of the multicomponent precursor system were further evaluated through exposure window analysis for patterning dense and semi-dense
features. An exposure window provides the range of doses for a particular line and space pitch which minimizes the difference between the printed and target dimensions. Ideally, one desires a large exposure processing window where changes in imaging doses have minimal impact on the patterned dimension. However, low and high exposure doses can result in patterned linewidths that are small and large in a negative tone system such as the metal-organic imaging scheme, respectively. The linewidth bias is typically quantified by patterning lines and spaces of varying pitches to determine the range of exposure doses where the target dimension can be patterned to satisfaction. Figure 3-13 plots the measured dimension of lines and spaces for desired features of 500 and 1000 nm in a dense 1:1 line and space pitch at various exposure doses. As expected, the dimension of the line increases with higher exposure dosage due to longer dwell times by the electron beam. Typically, the exposure window is defined as the dose variation for a +/- 10% change in critical dimension. For the 500 and 1000 nm 1:1 dense line/space patterning, the exposure window ranges from about 120-134 µC/cm² and 112-128 µC/cm², respectively. The exposure window is approximately 15 µC/cm² for both 500 and 1000 nm dense patterning. However, a narrower exposure window would be expected for smaller patterning dimensions. Further, Figure 3-14 plots the exposure windows for various line/space pitches of 500 and 1000 nm features. It can be seen that the exposure window for the 500 and 1000 nm isolated patterns of 1:4 lines/space pitch ranges from about 128-176 µC/cm² and 100-130 µC/cm², respectively. The exposure window widens as the patterns become separated for larger pitches. Mainly, the exposure window range from about 15-30 µC/cm² for patterning of various pitches with the multicomponent precursor.
Figure 3-13: Exposure window for 1:1 line:space pitch for a 200 nm thick multicomponent precursor film for target dimensions of 500 and 1000 nm.

Figure 3-14: Exposure windows for 1:1, 1:2, and 1:4 line:space pitch for a 200 nm thick multicomponent precursor film for target dimensions of 500 and 1000 nm.
Bilayer imaging of the multicomponent precursor was also investigated on top of a hard baked novolac (2 hours, 180°C) planarizing layer. A precursor film thickness of 200 nm was spin coated on top of the 442 nm thick hard baked novolac film. After preparing the bilayer film stack, line and space patterns were printed at 160 μC/cm² on a 1:4 pitch at 20 keV accelerating potential. After wet development of the imaging layer in MIBK for 30 seconds, the film was thermally converted at 180°C for 10 minutes to avoid film shrinkage of the etch mask during pattern transfer. Next, the pattern was transferred to the substrate using an O₂/Ar plasma. Figure 3-15 shows the top-down and tilted images before and after the pattern transfer. It can be seen that the features degraded during the etch transfer process through the hard baked novolac layer. A similar kind of phenomena was also observed during the bilayer patterning of the titanium carboxylate precursor on top of hard baked novolac. Again, the degradation in the features is likely due to the thermal processing performed prior to pattern transfer in order to eliminate unconverted organic material from the precursor film. Thus, during the pattern transfer process the features relieve stress through formation of wavelike patterns. Also, it has been observed that without thermal processing prior to pattern transfer that redeposition of the etch mask onto the wafer causes formation of debris in the unexposed regions that is undesired. Thus, a tradeoff between redeposition and stress relief exists for bilayer processing of these materials.
Figure 3-15: Top down and tilted SEM micrographs showing developed (left) and pattern transferred (right) images for a bilayer lithography process of the multicomponent Ba:Sr:Ti precursor on top of hard baked novolac.
3.4. Summary and Conclusions

In this chapter, we have developed and characterized dual and multicomponent metal-organic precursors that are viable as inorganic resists for electron beam lithography. The metal-organic imaging approach has been extended from the single component titanium precursor systems to the dual component barium:titanium and multicomponent barium:strontium:titanium systems. The barium and strontium precursors are carboxylate based precursors that are compatible with the titanium precursors based on carboxylates and alkoxides. Previously, the alkoxide based titanium precursor was found to be hydrolytically unstable by itself but in the presence of the barium and strontium precursors provides a stable precursor film that could utilized for high resolution lithography.

The consequences of incorporating such high atomic number precursors on lithographic parameters was thoroughly investigated. The electron beam imaging properties of the precursor film was enhanced due to a higher secondary electron yield provided by the incorporation of the high atomic number atom into the precursor matrix. A large enhancement in sensitivity was observed as the barium and strontium precursors were incorporated. However, a critical limit was also observed for the addition of these high atomic number precursors beyond which the imaging properties were not enhanced. For the barium:strontium dual component system, a 1:1 molar ratio was found to be optimal. Also, for the multicomponent barium:strontium:titanium system, minimal differences were noticed between the 1:1:1 and 1:1:2 molar mixtures of the precursors. With the addition of the barium precursor to the titanium, the sensitivity was enhanced by about 340 µC/cm² for a 1:1 molar ratio at 10 keV accelerating potential. Further, increasing the effective atomic
number of the precursor film through the addition of the strontium precursor in a 1:1:1 molar ratio enhanced the sensitivity by another 100 µC/cm². Also, the etch selectivity between hard baked novolac and the multicomponent ba:sr:ti precursor was a factor of two greater than that of the single component titanium precursor system. The addition of these high atomic number precursors decreases the volatility of the etch products during plasma processing. The high resolution capability of the multicomponent precursor system was demonstrated by patterning 100 nm features in a 200 nm thick precursor film on top of a silicon substrate. The process exposure window for dense and isolated patterns was also characterized. However, bilayer structures of the precursor film on top of hard baked novolac with high aspect ratios were found to lack pattern fidelity. The primary cause of the distorted patterns is stress relief during post patterning thermal processing that improves the etch resistance of the patterns. However, the stress build up during the thermal processing is relieved during plasma processing that causes pattern distortions.
4. DEVELOPMENT OF AN ALTERNATIVE INORGANIC ELECTRON BEAM RESIST: ENHANCING THE ELECTRON BEAM SENSITIVITY OF HYDROGEN SILSESQUIOXANE (HSQ)

4.1. Introduction

In recent years, interest in electron beam lithography has steadily increased as both (1) a lithography solution that can meet the high resolution patterning demands for sub-70nm node integrated circuit device generations and (2) a direct write patterning method that can be used to manufacture advanced photomasks (i.e. masks requiring optical proximity correction, phase sifting, etc.) required for low wavelength optical lithography. In the first case, electron beam lithography has been proposed as an alternative to optical lithography due to its superior resolution capabilities that would allow extension of Moore’s law type scaling into future device generations. The major hindrance for integration of electron beam lithography into a high volume semiconductor manufacturing environment has been the extremely low wafer throughput that is possible with conventional direct write electron beam systems. In order to be sufficiently productive, a method for extending from the typical raster electron beam scanning process to a massively parallel mode of operation is required. One approach is to utilize a tool employing large arrays of beams writing simultaneously, and such methods have
been explored for both microcolumn array systems and for hybrid laser-photocathode-electron beam column systems. However, a more popular route that has been explored by a number of different investigators is the idea of a projection electron beam system. In projection electron lithography systems, in an analogous fashion to optical lithography, a patterned mask is illuminated by a large electron beam and backscatters electrons striking undesired locations while thin membrane regions transmit electrons in the desired regions of exposure. The transmitted pattern of electrons is then focused down onto a wafer using an electron beam focusing column. This approach has been under investigation and development for over a decade, and significant recent progress has been made in demonstrating the feasibility of both projection electron beam lithography tools and massively parallel beam systems that would drastically improve the throughput of electron beam methods to levels comparable to that of optical lithographic systems\(^{70,71,72}\). Alongside the development of higher throughput electron beam systems such as the projection tools just mentioned, classical direct write electron beam lithography has sustained a niche market in semiconductor manufacturing as both a method for patterning in device prototyping work and as the primary method for fabricating high resolution photomasks used in optical lithography\(^{73}\). The ability to place patterns to within an accuracy of approximately 1 nm and to produce the high feature resolutions required by optical enhancement methods (e.g. optical proximity correction) has allowed for the continued fabrication of high precision photomasks that are difficult or impossible to produce using optical pattern generators. In addition, electron beam lithography has more recently been applied to the fabrication of imprinting templates used for step and
flash imprint lithography, a 1X lithography method that places high demands on the ability to make precision masks.\textsuperscript{74}

With this proliferation of electron beam lithography in mainstream semiconductor manufacturing, numerous research groups are exploring viable electron beam resist processes suitable for high resolution patterning.\textsuperscript{75} Recently, a resist process developed by Namatsu showed the feasibility of using hydrogen silsesquioxane (HSQ) (see Figure 4-1) as a high resolution negative tone electron beam resist.\textsuperscript{76} HSQ is an oligomer containing a mixture of the caged silsesquioxane molecule along with a linear crosslinked network. Traditionally, HSQ has been used as a low dielectric constant spin on glass for the isolation of metal lines in back end of line processing.\textsuperscript{77,78} Typically, crosslinking of the polymer is achieved with temperatures above 400°C where the curing reaction proceeds through conversion of Si-H bonds to form Si-OH groups.\textsuperscript{79} These silanols are unstable and degrade to form siloxane bonds (Si-O-Si) whereby the caged structure is transformed into a network. A similar reaction occurs upon electron beam irradiation where silicon hydride (Si-H) bonds are scissioned to form silanols (Si-OH) in the presence of absorbed moisture within the film. These silanol functionalities further decompose to form siloxane (Si-O-Si) bonds which render the exposed regions of the HSQ film insoluble in aqueous base. Since the discovery by Namatsu in 1998, this resist process has been applied in single and bilayer lithography schemes for various applications. Using a single layer resist process, Mollard demonstrated fabrication of 20 nm polysilicon gates during the buildup of a conventional metal-oxide semiconductor field effect transistor (MOSFET).\textsuperscript{80} Further, due to its high etch resistance in an oxygen plasma, HSQ has been utilized in a bilayer lithography process with a hard baked novolac
planarizing layer\textsuperscript{81}. Using this bilayer approach, aspect ratios on the order of 30:1 have been demonstrated after pattern transfer through the underlayer.

Even though this electron beam process has demonstrated very high resolution, a major drawback is the high electron beam dose required to cause network formation. For a 100 nm thick film exposed at 100 keV, an imaging dose of approximately 1500 \( \mu \text{C/cm}^2 \) is required to cause adequate modulation of the dissolution properties of the film to produce an image\textsuperscript{74}. Comparatively, chemically amplified resists (CARs) can be imaged with an order of magnitude lower dose in the range of approximately 100-200 \( \mu \text{C/cm}^2 \) for similar exposure conditions\textsuperscript{82}. In order to reduce the exposure dose required to print HSQ and to make it comparable to that of CARs, it would be attractive to modify the imaging scheme for HSQ to operate in a catalyzed manner similar to that of a CAR. Recently, Harkness demonstrated a strategy in which a photobase generator (PBG) was used to catalyze network formation in order to optically pattern HSQ at DUV wavelengths\textsuperscript{15}. It was also shown that increasing the PBG loading in an HSQ-PBG mixture enhanced the optical sensitivity of HSQ\textsuperscript{83}. This approach takes advantage of the rapid conversion of the silicon hydride (Si-H) group to a silanol (Si-OH) in the presence of absorbed moisture and a base catalyst. The photobase generators used by Harkness and coworkers possessed large extinction coefficients in the DUV region which made optical patterning possible. In this work, one of the goals was to explore the extent to which the electron beam sensitivity of HSQ could be enhanced by the use of a similar approach. Also, an alternative approach for enhancing the sensitivity of HSQ is through a dual processing method that utilizes pre-exposure thermal baking to obtain partial conversion was also investigated. As mentioned previously, these silsesquioxane
materials are most commonly thermally processed at 400°C in order to obtain the low dielectric constant properties of the polymer. Therefore, a dual processing approach with an initial thermal conversion step prior to electron beam exposure could be utilized to reduce the electron beam imaging doses. A similar method was also exploited in the metal-organic imaging scheme where it was found that the contrast of the patterning film decreased with increasing thermal conversion. A similar result would also be expected in this study where sensitivity enhancement is achieved at the expense of contrast due to the non-differentiative nature of thermal processing.

In this chapter, the two different methods of enhancing the electron beam sensitivity of HSQ were studied in detail. First, the effects of thermal processing on enhancing the electron beam sensitivity were studied through various pre and post-exposure thermal treatments. It was generally found that the sensitivity could only be enhanced modestly with decreased imaging contrast. Secondly, the consequences of adding sensitizer compounds for enhancing the electron beam sensitivity of HSQ were studied. Both a photobase generator and a photodecomposable base were studied as sensitizers. The effects of different post exposure bake temperatures and bake times on sensitivity and contrast of these mixtures were studied. In particular, enhancement in printing doses of single pixel wide lines with and without the sensitizers was compared. Further, it is known that silicon hydride bonds are susceptible to hydrolysis which can cause gradual network formation in solution and the addition of sensitizers might be detrimental to shelf life. Thus, the influence of sensitizers on network formation and solution stability was evaluated and characterized.
4.2. Materials and methods

Hydrogen silsesquioxane (Fox-15) in methyl isobutyl ketone (MIBK) with a solids content of 22 wt% was purchased from Dow Corning, Midland, MI. The solution was further diluted with MIBK to 3 wt% solids in order to obtain thin films. HSQ films were spin coated onto silicon substrates using a CEE 100 spinner and soft baked at 110°C for 90 seconds to remove excess solvent. After coating, film thicknesses were measured using an M-2000V ellipsometer from J.A. Wollam, Inc, Lincoln, NE. Ellipsometric spectra were obtained in the wavelength range of 370 to 1000 nm with a spacing of approximately 3 nm at three different incident angles of 65°, 70°, and 75°. The collected ellipsometric data was fitted using a standard Cauchy layer model for the HSQ film and a bulk silicon model for the substrate to obtain thickness and refractive index profiles for the films.

In the following studies, triphenylsulfoniumhydroxide (TPS-OH) and nitrobenzylcarbamate (NBC) were used as possible electron beam sensitizers. Both sensitizers were purchased from Midori Kagaku Co. Ltd., Japan, and their molecular structures are shown in Figure 4-1. TPS-OH is a photodecomposable base (PDB) that is commonly used in resist formulations to improve shelf life, stability against airbone molecular contamination, and latent image quality\textsuperscript{84}. In the case of optical resists, the TPS-OH base is decomposed to form neutral fragments in the exposed regions but acts as an acid scavenger to neutralize acid molecules diffusing into the unexposed regions\textsuperscript{85}. However, it also neutralizes a small amount of acid generated in the exposed regions and thus reduces the resist sensitivity. In the case of addition of TPS-OH to HSQ, it is
expected that it may be possible to form a positive tone system in the mixed TPS-OH/HSQ system. This would occur because the TPS-OH would be expected to catalyze network formation in the HSQ at lower temperatures than would be possible in pure HSQ alone. However, in regions of the TPS-OH/HSQ film where it is exposed to the electron beam and the TPS-OH is decomposed, no such catalytic activation of the network formation reaction would occur. Thus after e-beam exposure, the film could be baked which would promote network formation at a faster rate and at lower temperatures in the unexposed regions, thus making the unexposed regions insoluble as the Si-O-Si network is formed and thereby producing a positive tone image.

NBC is a typical example of an amine based PBG derived from a large family of photolatent bases of carbamates. In these PBG compounds, the primary photochemical event is an excitation of a nitro group resulting in an abstraction of the benzyl hydrogen followed by structural rearrangement to produce a basic amine functionality. Therefore, in mixed NBC/HSQ systems, the regions of the film exposed to the electron beam will contain the amine base which will in turn catalyze the network formation of the HSQ reaction, thus leading to negative tone image formation. Both of these possible sensitizer compounds were loaded into HSQ solutions at 5 wt% with respect to total solids. It should be noted that the solubility of TPS-OH in the MIBK-HSQ solutions was much lower than that of NBC, and that higher loadings for TPS-OH were not possible.
All electron beam exposures were performed using a JOEL 5910 SEM (JEOL Ltd., Tokyo, Japan). Electron beam focus and astigmatism were optimized using evaporated gold on polished pyrolytic graphite samples purchased from E.F. Fullam, Inc, Latham, NY. All exposures were performed at an accelerating potential of 25 keV using a 10 pA emission current. For high resolution electron beam lithography, single pixel wide lines with a pixel spacing of 20 nm were printed. For contrast curve measurements, dose arrays of 10 micron square pads were exposed, developed, and their step heights were measured using a Dimension 3100 atomic force microscope with a Nanoscope IIIa
controller (Digital Instruments, Santa Barbara) operated in tapping mode. Finally, SEM images of isolated lines were obtained using a Hitachi 3500 SEM after depositing a thin layer of gold on the surface to prevent charging.

4.3. Results and Discussion

4.3.1. Processing delay effects

It was first observed by van Delft that delays in processing of HSQ could have detrimental effects on its electron beam imaging properties. Processing delays in coating, exposure, and development were found to decrease the exposure doses required for imaging. It is well known in silicone chemistry that the silicon hydride functionality is susceptible to hydrolysis, which can cause the transformation from the HSQ cage structure to its insoluble network structure. As a consequence of networking induced by hydrolysis during processing delays, contrast was also found to decrease for delays in coating and development but to increase for a delay in exposure. Similar degradation behavior was observed in this study where the dose to print decreased with delays in coating and exposure. The electron beam imaging curves for processing delays in coating are plotted in Figure 4-2. Here, the sensitivity is defined as the dose to remove half of the original film thickness and contrast as a best linear fit between 0 and 60% of the normalized remaining thickness versus log(dose) curve. HSQ solutions processed
after 30 and 180 days exhibited sensitivities of 55 and 16.5 $\mu$C/cm$^2$, respectively. Also, the contrast decreased from 3.32 to 1.86 over the 150 day delay in processing. This observation of higher sensitivity and lower contrast is indicative of gradual degradation of the caged silsesquioxane molecule to the insoluble siloxane network occurring within the solution. Further, Figure 4-3 illustrates the effect of a 24 hour exposure delay after spin coating. The films were kept in a 30% relative humidity environment at room temperature during this period. As expected, the dose required to print images in the material decreased from 16.5 to 13 $\mu$C/cm$^2$ as a consequence of hydrolysis in the solid film during the exposure delay. This delay also resulted in a decrease in contrast from 1.86 to 1.35. The result is different from that reported in the study performed by Delft where contrast was observed to increase with a delay in exposure. The decrease in contrast observed in this work would be consistent with partial condensation and network formation throughout the film as a result of hydrolysis since such conversion leads to a loss of chemical contrast (i.e. smaller differential change in solubility possible with exposure). Again, these results confirm that the siloxane network formation occurs within the coated film as well as in solution. The rate of the network formation is much faster in the coated films since they were maintained in a high relative humidity condition while the solution was stored in low humidity in a freezer. Due to these hydrolytic instabilities with processing these materials, in the remaining studies reported in this work, films were coated, exposed and developed with as little delay as possible (typically on the order of minutes).
Figure 4-2: Electron beam response curves showing the effects of delays in processing HSQ solution after 30 and 180 days.

Figure 4-3: Electron beam response curves showing the effects of a 24 hour exposure delay after spin coating of HSQ films.
4.3.2. Enhancing the electron beam sensitivity of HSQ: dual processing approach

The most facile approach for enhancing electron beam imaging characteristics of HSQ is through dual processing where a thermal cure is combined with electron beam patterning. A partial transformation of the silsesquioxane cage/network can be achieved through thermal treatments for accelerating the imaging process. Silsesquioxane materials are most commonly processed via thermal curing in a range of temperatures between 200 to 450°C and much research has been performed on understanding the thermal curing process\textsuperscript{87,88}. Several authors have proposed that thermal curing of HSQ proceeds in four important stages: (1) solvent loss from room temperature up to 200°C, (2) cage/network redistribution from 200-350°C, (3) thermal disassociation of Si-H and cage/network redistribution from 350-425°C, and (4) finally, breakdown of the pore structure for processing temperatures above 450°C\textsuperscript{89}. The silsesquioxane transformation reaction can be followed through infrared spectroscopy that monitors the vibrational transitions in the bonding modes of the Si-O and Si-H functionalities. It has been observed that the absorbances corresponding to the Si-H and Si-O bonding modes of the caged silsesquioxane and Si-O bonding mode of the linear network decrease and increase in concentration as thermal curing proceeds, respectively. That is, the thermal curing proceeds through dissociation of the silicon hydride linkages to cause the transformation of the silsesquioxane cage to the network as inferred from the transition in absorbances of the Si-O bonds before and after conversion. It has been shown by Liu and coworkers that structural differences in the cage/network matrix is evident for baking temperatures as low at 80°C when compared to an as coated film\textsuperscript{89}. The results observed by Liu are not
due to the evaporation of solvent from the film since the absorption of the casting solvent MIBK is well outside of the Si-O and Si-H excitation regions where the structural changes were monitored. Further, it has been recognized by different authors that minimal changes in the structural confirmation occur during electron beam irradiation for lithographically useful imaging doses \(^{76,86}\). That is, minimal changes in the infrared spectra are observed before and after electron beam exposure of the films are irradiated to nominal electron beam patterning doses. The structural changes are only observed in silsesquioxane films after exhaustive electron beam conversion. These observations indicate that few imaging events are needed under the action of an electron beam to render the silsesquioxane film insoluble in an aqueous base.

In this study, post apply baking (PAB) and post exposure baking (PEB) were investigated as possible thermal treatment procedures for accelerating the electron beam imaging characteristics of HSQ. PAB and PEB treatments at 150, 175, and 200°C for a duration of 1 minute each were investigated. Figure 4-4 plots the electron beam response curves for the various PAB thermal treatments. It can be observed that minimal enhancement in imaging reactions were obtained for the various PAB treatments. The electron beam sensitivity exhibited by HSQ for PAB's at 150, 175, and 200°C were 67.6, 67.5, and 59.5 \(\mu\text{C/cm}^2\), respectively. Even though a minimal enhancement in sensitivity was observed with a PAB treatment of 200°C, the thermal baking reduced the contrast of the resulting matrix. The contrast decreased by about 0.2 as the PAB treatment temperature was increased from 150 to 200°C. It would be expected that the imaging reaction could be further enhanced with increasing PAB temperatures or thermal baking times at a particular temperature but only at the cost of reduced contrast. Again, the
contrast decreases due to a lower difference in the chemical makeup of the exposed and unexposed regions created by the blanket conversion to the network form induced by the thermal treatment. Overall, the use of PAB's had minimal impact on enhancing the imaging performance of silsesquioxane based films. Further, the effects of PEB's at 150, 175, and 200°C for a duration of 1 minute each was also investigated. The exposed samples were removed from the electron beam chamber after venting and immediately transferred to the hot plate for post exposure baking. Figure 4-5 plots the electron beam response curves for the different PEB thermal treatments. It is observed that the PEB's were much more effective than PAB's in enhancing the electron beam imaging characteristics of HSQ. The sensitivity was enhanced by about 14 \( \mu \text{C/cm}^2 \) as the PEB treatment temperature was increased from 150 to 200°C. As expected, the contrast decreased with increasing PEB temperatures due to blanket conversion which reduces the ratio of dissolution between the exposed and unexposed regions. A difference in contrast of about .2 was observed between PEB treatments at 150 and 200°C. Again, the sensitivity can be further enhanced with higher thermal baking temperatures or longer thermal bake times but only at a cost of reduced contrast. With this dual processing approach, it has been primarily shown that PEB thermal treatments were much more effective than PAB thermal treatments in improving the electron beam imaging performance of HSQ but alternative methods with larger enhancements in sensitivity while maintaining contrast are desired.
Figure 4-4: Electron beam response curves for various PAB thermal treatments prior to electron beam exposure.

Figure 4-5: Electron beam response curves for various PEB thermal treatments after to electron beam exposure.
4.3.3. Enhancing the electron beam sensitivity of HSQ: sensitizer catalyzed imaging approach

An alternative approach for enhancing the electron beam imaging characteristics is through incorporation of sensitizers into the silsesquioxane matrix that promote the critical cage to network transformation and redistribution reactions. It is known in silicone chemistry that sensitizers can function as catalysts that enhance imaging reactions through participation in the conversion of silicon hydride linkages to the desired insoluble siloxane crosslinked functionalities. The sensitizer catalyzed imaging scheme was first applied to HSQ in an effort to render the silsesquioxane matrix optically definable at DUV wavelengths. Silsesquioxanes exhibit minimal absorption at DUV wavelengths of 193 and 248 nm but the inclusion of sensitizer with high absorption in this wavelength regime could be utilized to pattern the matrix. Harkness demonstrated this approach by incorporating photobase generators that exhibit high extinction coefficients at DUV wavelengths to pattern micrometer sized features. It was postulated that the conversion of the caged species to the insoluble network proceeds through rapid hydrolysis of the Si-H to Si-OH functionalities which can further condense to form the insoluble Si-O-Si siloxane network. Even though photobase generators are intended to be activated through excitations from photons, energy transfer from electron beams could also be utilized to decompose them into their ionic species.

The consequences of including sensitizers in silsesquioxane matrices might strongly depend upon the hydrolysis state of the silsesquioxane solution. As previously mentioned, the silsesquioxane cage is prone to self hydrolysis which alters the imaging
characteristics of the HSQ solution during storage. The concentration of Si-H and Si-OH functionalities decreases and increases during the lifetime of the HSQ solution, respectively. The variation in the hydrolytic state of the solution could affect the performance of the sensitizer if a preference exists for either catalyzing the hydrolysis or condensation reactions. It would be ideal if the sensitizer is capable of catalyzing both the hydrolysis and condensation reactions necessary in the transformation of the caged silsesquioxane to the linear insoluble siloxane network. However, it is possible that only one of the reactions, either hydrolysis of silicon hydride functionalities or condensation of silanol groups to form the insoluble siloxane, is catalyzed. Thus, the performance of the sensitizer might change during the lifetime of the solution due to its evolving hydrolytic state. Further, the presence of sensitizers in a silsesquioxane medium could possibly accelerate the undesired hydrolysis reaction by participating as a catalytic medium for the nucleophilic attack by the water species. Therefore, the effect of including sensitizers in a silsesquioxane medium was investigated and its impact on imaging performance of fresh and aged solutions were studied and characterized in the following sections.

4.3.3.1. Effect of Loading Sensitizers into HSQ Solutions on Storage Stability

The primary reaction that transforms the silsesquioxane caged species is the conversion of the Si-H functionalities to Si-OH groups that further condense to form siloxane bonds (Si-O-Si). The structural transformation can be achieved through thermal curing and various forms of radiation including photons, electrons, and X-rays.\textsuperscript{90}
Undesirably, the conversion can also occur intrinsically in solution through the hydrolysis of Si-H to form Si-OH functionalities. This undesired dark reaction in solution modifies both the sensitivity and contrast of the resist as a function of shelf storage time due to the reduction in Si-H caged species concentration and formation of partial network structures. It is a concern that the addition of a sensitizer to the solution could have detrimental effects by enhancing the rate of these undesired dark reactions. Recently, in an effort to take advantage of the dark reaction, Ou and Chevalier reported on a rapid gelation process of HSQ using highly nucleophilic activating agents such as NH₄OH, formamide, polyethylene glycol, and γ–butyrolactone⁹¹. The proposed gelation mechanism is illustrated in Figure 4-6. In this reaction, the sensitizer behaves as a catalytic intermediary during the nucleophilic attack by a water molecule on a silicon atom containing a hydride linkage. Upon hydrolysis of the silicon hydride, the Si-OH functionalities can react with either Si-H or Si-OH groups in a rapid decomposition process to release water or H₂, respectively, and form the insoluble siloxane network (Si-O-Si). In their study, Lu and Chevalier observed that NH₄OH provided the fastest gelation times due to its highly nucleophilic character. Similarly, formamide and polyethylene glycol exhibited comparable gelation rates as both contain oxygen lone pair electrons which act as nucleophiles. The conclusions of their work were that the nucleophilicity and concentration of the activating agents strongly influence the rate of network formation.
Figure 4-6: Proposed mechanism of conversion of Si-H groups to form Si-O-Si bonds through attack by water with a catalytic nucleophile (Nu).

In this study, the two possible sensitizers investigated to enhance the electron beam imaging characteristics of HSQ exhibit vastly different nucleophilic behavior. Even though TPS-OH is a photodecomposable base, it behaves as a poor nucleophile due to the steric hindrance of the phenyl groups attached to the sulfur center. Comparatively, NBC can function as a better nucleophile since it contains lone pair electrons on both the oxygen and nitrogen atoms. Therefore, NBC would be expected to affect the rate of hydrolysis to a much greater extent than TPS-OH due to its higher nucleophilicity. In order to study the effects of the addition of TPS-OH and NBC to HSQ on the long term stability of HSQ solutions, electron beam imaging doses for pure HSQ and the mixtures were monitored over a period of 6 months. Figure 4-7 compares the electron beam
contrast curves of HSQ, HSQ/TPS-OH, and HSQ/NBC films prepared and processed from solutions after approximately 25 weeks delay from the time sensitizers were added to the HSQ solution. The HSQ solution exhibited a sensitivity and contrast of approximately 55 µC/cm² and 3.32, respectively, at the start of the experiment. These solutions were maintained in polypropylene bottles in a dry freezer at 0°C and the sensitizer loading was 5 wt% with respect to total solids. After 25 weeks, the sensitivity and contrast exhibited by the pure HSQ were 16.5 µC/cm² and 1.86, respectively. The sensitivity and contrast of the HSQ/TPS-OH film imaged without a post exposure bake were 30 µC/cm² and 1.93, respectively. The sensitivity and contrast exhibited by the HSQ/NBC film without a PEB were approximately 15 µC/cm² and 1.80, respectively. Thus, not only does the presence of TPS-OH not accelerate the hydrolysis and condensation of HSQ, it appears to slow down the rate of formation of the siloxane network in solution. However, as might be expected, the inclusion of NBC appears to have slightly accelerated the conversion of the Si-H groups in solution to form partial siloxane networks, thus leading to the lower required imaging dose for that mixture.
The addition of a sensitizer to a silsesquioxane medium has been shown to affect the undesired hydrolysis dark reaction. The rate of enhancement of the reaction is primarily dependent upon the nucleophilicity of the sensitizer. Therefore, it is clear that one must be judicious when adding a sensitizer to HSQ and proposing to store it for long periods of time since it may have detrimental effects in terms of accelerating siloxane network formation in solution. Surprisingly though, TPS-OH did act as a stabilizer for HSQ, and this fact may be exploited in the design of future accelerated HSQ or HSQ-like systems. It is possible that the hydrolysis of silsesquioxane results in silanol formation.
which may be stabilized against condensation by TPS-OH. It is known that TPS-OH binds strongly to hydroxyl sites in phenolic systems such as polyhydroxystryrene\textsuperscript{85}. Figure 4-8 illustrates this association between the TPS-OH cation and the phenolic site of a polyhydroxystryrene. A similar type of association between TPS-OH and silanol sites on the silsesquioxane molecules could retard the further condensation and formation of the insoluble siloxane bonds.

Figure 4-8: An illustration of binding between a TPS-OH cation and a hydroxyl site on a polyhydroxystryrene ring.
4.3.3.2. Enhanced electron beam imaging with a photodecomposable base

As previously mentioned, TPS-OH is a photodecomposable base which undergoes decomposition into neutral fragments upon excitation. The photolytic decomposition mechanism of TPS-OH is illustrated in Figure 4-9 and a similar degradation mechanism is assumed for electron beam irradiation\(^\text{95}\). Upon energy transfer, the triphenylsulfonium cation produces a proton through cleavage of a phenyl ring. Next, the protonated sulfur abstracts hydrogen from the phenyl radical and is attacked by the hydroxide ion in order to generate a neutral sulfur compound and water. It is possible that the neutral sulfur compound could then function as a nucleophile in catalyzing the conversion of the Si-H groups to Si-OH and the condensation of the resulting silanol functionalities by virtue of its two lone pairs of electrons. In addition, it is also possible that the production of water during the decomposition of the TPS-OH may also serve to accelerate hydrolysis of the Si-H groups to form Si-OH groups, which subsequently condense to form the siloxane network.

**Figure 4-9:** Decomposition mechanism of triphenylsulfonium hydroxide (TPS-OH) to generate a nucleophillic neutral sulfur species.
The consequences of addition of TPS-OH in a silsesquioxane medium was investigated in fresh and aged HSQ solutions in order to determine the ability of the sensitizer to affect the rates of the hydrolysis or condensation reactions. In a fresh HSQ solution, the concentration of silicon hydride functionalities is much higher as compared to the silanol functionalities that the TPS-OH can possibly associate itself with. Thus, in a fresh HSQ solution, the affects of the PDB will be mainly in accelerating the hydrolysis reaction of the Si-H functionalities. Figure 4-10 shows the electron beam response curves for films treated with and without PEB treatments. All of the film thicknesses were maintained at about 100 nm and the loading of the TPS-OH was 5 wt%. It can be observed that the loading of the TPS-OH had a minimal impact on the enhancement of imaging properties of fresh silsesquioxane solutions. The sensitivity was enhanced by about 15 µC/cm² for a PEB at 200°C as compared to a film without a PEB treatment. Also, the contrast is observed to decrease slightly from 3.1 to 2.4. Again, these observations indicate that the PDB has a minimal impact on the imaging performance of the fresh silsesquioxane matrix. Further, the enhancement in sensitivity could also be due to the thermal treatment performed immediately after electron beam exposure that was previously illustrated. The impact of the PDB on imaging an aged HSQ solution was also investigated wherein a higher concentration of silanol functionalities exist due to the hydrolysis of the solution which gradually occurs over time. Figure 4-11 plots the various response curves for 5 wt% aged TPS-OH loaded HSQ films with PEB temperatures of 125°C, 150°C, 175°C, and 200°C. All film thicknesses were maintained at approximately 100 nm and post exposure bakes were performed for one minute immediately after venting the electron beam chamber and removing the sample from the
sample holder. Without a post exposure bake, the TPS-OH loaded HSQ exhibits a sensitivity of 30 \( \mu \text{C/cm}^2 \) with a contrast of 1.93. With a PEB of 125\(^\circ\)C, a slight enhancement of sensitivity to 25 \( \mu \text{C/cm}^2 \) is observed with a similar contrast of 1.93. However, with higher PEB temperatures drastic improvements in sensitivity are observed. For a PEB temperature of 150\(^\circ\)C, the sensitivity is enhanced by two-fold to approximately 15 \( \mu \text{C/cm}^2 \) with an increased contrast of 2.34. For a PEB temperature of 175\(^\circ\)C, the sensitivity is again enhanced by two-fold to 8.5 \( \mu \text{C/cm}^2 \) with a contrast of 1.83. PEB temperatures above 175\(^\circ\)C resulted in no further enhancement of the sensitivity beyond approximately 9 \( \mu \text{C/cm}^2 \), and these higher temperatures caused a marked decrease in contrast. Mainly, it has been found that the impact of the PDB on enhancing the electron beam imaging characteristics is much greater for an aged solution. It can be concluded that the TPS-OH sensitizer has a much greater impact on the condensation reaction that results in the formation of the insoluble siloxane network.
Figure 4-10: Electron beam contrast curves for different post exposure bake temperatures with 5 wt% TPS-OH loaded fresh HSQ films.

Figure 4-11: Electron beam contrast curves for different post exposure bake temperatures with 5 wt% TPS-OH loaded aged HSQ films.
The aforementioned studies have compared the sensitivity and contrast with and without the loading of the photodecomposable base in HSQ by exposing 10 µm square pads. Of more interest perhaps is a comparison of the impact of adding such a compound on the high resolution patterning performance of HSQ, and thus the imaging doses required to print a single pixel wide electron beam exposures were investigated in both pure HSQ and the HSQ/TPS-OH mixture. The loading of the PDB was maintained at 5 wt% and the thickness of the films was approximately 100 nm. Figure 4-12 compares SEM pictures of identical exposure arrays performed for the HSQ films with and without the loading of TPS-OH. A PEB at 175°C for 1 minute was performed for the TPS-OH loaded HSQ film while a PEB was not performed on the HSQ film. The exposure doses ranged from 50 µC/cm² to 850 µC/cm² with an increment of 50 µC/cm². For the HSQ film without any loading of the TPS-OH, the dose required to print a line is approximately 300 µC/cm². However, for the HSQ film loaded with the TPS-OH, the printing dose is reduced to only 100 µC/cm², representing a reduction of almost 70% in the required imaging dose.

![Figure 4-12: Single line exposures performed on HSQ films with (right) and without (left) the 5wt% loading of TPS-OH at 25 keV accelerating potential with a 100 nm nominal film thickness. The exposure doses was varied from 50 to 850 µC/cm² with an increment of 50 µC/cm².](image)
4.3.3.3. Enhanced electron beam imaging with a photobase generator

Typically, PBG materials decompose to generate a neutral base compound that can be used for a variety of purposes such as inducing crosslinking within a resist. The photolytic decomposition mechanism of NBC is illustrated in Figure 4-13\textsuperscript{85}. The decomposition is initiated through intramolecular hydrogen abstraction from an excited nitro group. The generated radial is redistributed to form an stable benzylic ether, carbon dioxide, and the desired amine base. Again, it is also assumed that a similar degradation mechanism is followed upon electron beam irradiation of this compound. With this scheme, the amine base can participate as a catalyst during the transformation steps of the isolated HSQ cage molecules into the siloxane network required for patterning HSQ by accelerating the imaging reaction.

![Figure 4-13: Decomposition mechanism of nitrobenzylcarbamate (NBC) to generate an amine base.](image)

The consequences of adding the PBG into a silsesquioxane matrix were again studied for varying hydrolytic states of the medium. As mentioned previously, the
availability of silanol functionalities increases during the lifetime of the solution whereby affecting the performance of the catalytic species. It is conceivable that the condensation reaction is much more impacted through the addition of the sensitizer as compared to the hydrolysis reaction which was observed with the photodecomposable base. In order to investigate this phenomenon, fresh and aged silsesquioxane solutions containing the carbamate based sensitizer were evaluated. Figure 4-14 shows the electron beam response curves for a freshly mixed solution containing the sensitizer for various thermal treatments after electron beam exposure. Again, it was observed that the inclusion of the PBG had minimal impact on enhancing the electron beam imaging characteristics of the film. The sensitivity of the PBG loaded HSQ films processed with a PEB treatment at 150, 175 and 200°C are 60.2, 52.5, and 49.2 μC/cm², respectively. The sensitivity was enhanced only by about 10 μC/cm² for a PEB at 200°C but a part of this enhancement could be due to direct thermal acceleration as well. These results indicate that the sensitizer has minimal impact on enhancing the electron beam imaging performance of fresh HSQ solutions contain the maximum concentration of the silicon hydride functionalities. That is, the sensitizer is not effective in participating in the hydrolysis reaction that converts the silicon hydride to a silanol functionality that eventually condenses to form the insoluble network that is desired for improving the patterning characteristics of HSQ. The observations are analogous to the sensitized version containing the photodecomposable base which indicates the difficult in enhancing the electron beam imaging of fresh silsesquioxane mediums.
The thermally catalyzed conversion of an aged HSQ solution containing NBC as a sensitizing agent was investigated at post exposure thermal bake temperatures of 150°C, 175°C, and 200°C. In this experiment, film thicknesses were maintained at 85 nm with a sensitizer loading of 5 wt% with respect to total solids and a PEB time of 1 minute was used in all cases. The electron beam contrast curves are plotted for the various PEB temperatures in Figure 4-15. With a PEB at 150°C, the NBC loaded HSQ film exhibited a sensitivity and contrast of 75 µC/cm² and 2.46, respectively. At this PEB, minimal enhancement of sensitivity as compared to pure HSQ is observed which exhibited in the
case of these solutions a sensitivity and contrast of 80 $\mu$C/cm$^2$ and 2.56, respectively. The sensitivity and contrast for a PEB at 175°C were 56 $\mu$C/cm$^2$ and 2.09, respectively. At this PEB temperature, the sensitivity was enhanced by approximately 19 $\mu$C/cm$^2$ (~25% reduction in dose) while the contrast decreased as compared to the 150°C PEB. Finally, a PEB at 200°C enhanced the sensitivity to 35 $\mu$C/cm$^2$ while the contrast further decreased to approximately 1.64. Thus, for this PBG, it appears that temperatures in the range of and above 175°C are required to significantly accelerate the conversion of the Si-H functionalities for the formation of the siloxane network, but that a reduction in contrast for these high bake temperatures is experienced.

![Figure 4-15](image)

**Figure 4-15:** Electron beam response curves of NBC loaded old HSQ solutions thermally treated at 150, 175, and 200°C for 1 minute immediately after electron beam exposure.
Imaging of single pixel wide line electron beam exposures were again compared for a HSQ film with and without a 5 wt% loading of NBC using a 25 keV accelerating potential. Figure 4-16 compares SEM images of dose arrays in HSQ without a PEB, HSQ/NBC with a PEB at 175°C for 1 min, and HSQ/NBC with a PEB at 200°C for 1 min. In this experiment, the film thicknesses were also maintained at 85 nm and the exposure doses were varied from 50 $\mu$C/cm$^2$ to 850 $\mu$C/cm$^2$ with a spacing of 50 $\mu$C/cm$^2$. For pure HSQ, the printing dose is approximately 550 $\mu$C/cm$^2$. With a PEB of 175°C, the printing dose is further enhanced to approximately 300 $\mu$C/cm$^2$. Thus, the printing dose is reduced by approximately half as compared to pure HSQ. Finally, with a PEB of 200°C, the printing dose was decreased to only approximately 150 $\mu$C/cm$^2$. At this highest PEB temperature, the printing dose has been enhanced to only about one-quarter of the uncatalyzed pure HSQ. More detailed imaging studies are required to investigate the real impact of the possible loss of contrast on patterning performance when using such elevated temperature post-exposure bakes.
Figure 4-16: Single line exposures performed on HSQ, HSQ/NBC with a PEB at 175°C (middle), and HSQ/NBC with a PEB at 200°C (bottom) at 25 keV accelerating potential on 85 nm nominal film thickness. The exposure doses were varied from 50 to 850 µC/cm² with an increment of 50 µC/cm².
4.4. Summary and Conclusions

In this chapter, the ability to enhance the electron beam sensitivity of hydrogen silsesquioxane through pre- and post-patterning thermal treatments and through the addition of either triphenylsulfoniumhydroxide (TPS-OH, a photodecomposable base) or nitrobenzylcarbamate (NBC, a photobase generator) have been investigated. It was found the PEB’s were much more effective than PAB’s in enhancing the imaging properties but resulted in reduced contrast for increased thermal conversions. Also, only minimal enhancement in sensitivity was observed through thermal treatments for dual processing of these materials. Alternatively, it was found that both PDB and PBG compounds can act as sensitizers for HSQ and enhance the sensitivity of HSQ solutions. The impact of the sensitizer compounds were much more pronounced for aged HSQ solutions containing a higher concentration of silanol functionalities. Therefore, these sensitizers were much more effective in mediating the condensation reactions once the silanol functionalities are formed within the HSQ solution. However, with fresh HSQ solutions that contain a larger concentration of silicon hydride functionalities were not enhanced through the addition of sensitizer compounds. That is, the hydrolysis reaction that converts the silicon hydride to the silanol functionalities was not catalyzed by the sensitizers.

It was mainly found that the NBC-PBG promotes network formation through condensation of silanol functionalities formed during the aging of the silsesquioxane solution. Fresh silsesquioxane solutions mixed with the PBG did not show much enhancement in sensitivity. However, aged silsesquioxane/PBG solutions exhibited a
large enhancement in sensitivity due to catalyzation of condensation reactions. It was also found that the TPS-OH photodecomposable base improved the hydrolytic stability of the silsesquioxane solution through possible capping of the silanol functionalities that prevents further breakdown of the cage structure to form the crosslinked network. It was also found that aged silsesquioxane/TPS-OH solutions exhibited larger enhancement in sensitivity as compared to fresh silsesquioxane/TPS-OH solutions. It is believed that the chemical contrast between exposed and unexposed regions is improved by the capping of the silanol functionalities. Upon electron beam irradiation, the capping groups can be removed for inducing condensation and formation of the insoluble network.

The sensitivity of an aged HSQ was enhanced by more than 50% by using either sensitizers with an appropriate post exposure bake. However, decreases in contrast were observed with the higher post exposure bake temperatures required to achieve significant enhancements in the HSQ sensitivity using the sensitizers compounds. The enhancements in sensitivity are also partially due to the thermal acceleration from the baking that causes structural transformation of the silsesquioxane cage/network. The sensitizers utilized in this study were not strong nucleophiles that could cause rapid crosslinking within the solution medium. However, as mentioned previously, the use of strong nucleophillic agents were utilized to rapidly cure silsesquioxane based materials to form a gelled solution. It might be possible to incorporate an electron beam sensitive mildly nucleophilic agent in a fresh HSQ solution that could initiate curing reactions within the matrix even without the action of the electron beam. This kind of a system should be processed quickly in order to maximize the dissolution contrast between exposed and unexposed regions since the dark network formation would occur continuously with in
the solid state of the film. The main disadvantage of this process would be the necessity to prepare fresh solutions prior to processing and the choice of appropriate nucleophillic agents.
CHAPTER 5

5. CONSEQUENCES OF HIGH ATOMIC NUMBER SPECIES AND
NANOPARTICLES IN AN ELECTRON BEAM RESIST: A MONTE CARLO
STUDY

5.1. Introduction

Progressive miniaturization of semiconductor devices using optical lithographic pattern definition has been primarily brought about through reductions in the wavelength of light used to delineate patterns in a photoresist. At the present, the International Technology Roadmap for Semiconductors (ITRS) projects 157 nm F_2 lithography for the production of devices at the 65 nm technology node\textsuperscript{92}. Beyond 157 nm F_2 lithography, almost all organic materials will absorb the low wavelength irradiation and limit the penetration of light through photoresists. To overcome the strong absorption of low wavelength optical irradiation, next generational lithographic approaches such as extreme ultraviolet lithography (EUVL), electron beam projection lithography (EPL), ion beam projection lithography (IPL), and X-ray lithography (XRL) are being pursued to sustain miniaturization of semiconductor devices\textsuperscript{93,94,95,96}. Amongst these next generation lithographic technologies, electron beam lithography is the only approach that is currently being utilized extensively in semiconductor manufacturing. Direct write electron beam lithography is widely used in the industry for critical level high resolution photomask
fabrication. Unfortunately, the implementation of this raster scanning exposure technology in semiconductor manufacturing has been impeded by low wafer throughput. In order to achieve higher wafer throughput, a massively parallel transfer of patterning information to the resist is required. It has been recognized that projection electron beam lithographic approaches can be developed in close analogy to optical lithographic technologies which utilize a mask and focusing optics to project transmissive regions from the mask onto the wafer plane. In projection electron beam lithography a mask consisting of a patterned metallic scattering layer on top of a thin membrane is utilized. Electrons striking the metallic layer are backscattered into the electron column while those striking the thin membrane are transmitted to the resist for pattern delineation. Recently numerous advances have been made in demonstrating prototype projection electron beam lithographic tools such as PREVAIL and SCALPEL. Also, another unique approach being currently developed to increase the transfer of information in electron beam lithography has been through the use of a massive array of focused electron beams. It has been estimated that through the use of these methods, throughput can be enhanced to be on the order of optical lithographic systems.

With these exciting developments, new electron beam resist processes are being developed for the fabrication of future semiconductor devices. Electron beam resists are typically organic moieties containing atoms such as carbon, sulfur, oxygen, and hydrogen. Classical examples include acrylates, epoxies, sulfones, and chemically amplified resists. More recently, inorganic resists such as hydrogen silsesquioxane (HSQ), metal-organic precursors, and nanoparticle loaded organic resists are also being developed for electron beam lithography. Inorganic resists provide higher etch
resistance but exhibit much lower sensitivities as compared to organic resists. Typical printing doses of HSQ and metal-organic precursors are an order of magnitude higher than organic resists. In order to combine the high sensitivity property of an organic resist with the high etch resistance property of an inorganic resist, many researchers have included nanoparticles in an organic resist in order to obtain optimal performance. The nanoparticles most studied in detail so far have been fullerene and silica included in chemically amplified resist matrices\textsuperscript{105,106,107,108}. It has been shown that a 7 wt\% loading of silica in ZEP520® resulted in a twenty fold reduction of etch rate in an ashing oxygen plasma. Also, it has been postulated that a nanoparticle loaded resist enhances the mechanical resistance during wet development to prevent resist collapse.

The addition of the high atomic number species and nanoparticles in an electron beam resist changes the interaction between the impinging electrons and atoms in the resist film. The comparatively large atomic species exhibit different scattering behavior than the traditionally small atomic number atoms contained in an organic electron beam resist. The influence of high atomic number species and nanoparticles in an electron beam resist were studied in this chapter through Monte Carlo simulations. In order to isolate the effects of high atomic number species, a poly(methyl methacrylate) PMMA molecule was tagged with either a silicon or a titanium atom. Silicon and titanium were chosen to represent HSQ and titanium metal-organic precursor type resists, respectively. The consequences of adding these high atomic number species on scattering behavior as well as point electron distributions were characterized. In order to simulate a nanoparticle loaded organic resist, the film was considered as a two component system consisting of the resist and nanoparticle. Collisional probabilities between incident
electrons and the film were assigned according to the nanoparticle loading in the resist. Also, the film properties were calculated using a linear mixing rule of the polymer and nanoparticle properties. The validity of this linear mixing rule was studied through a percolative approach with random assignment of lattice sites as either a nanoparticle or a polymer. An incident electron was inserted randomly and the film properties were calculated as a function of distance away from the reference location in order to determine a critical threshold distance beyond which fluctuations in film properties are not observed. Therefore, Monte Carlo simulations were performed for incident electron energies where the average mean free path between successive collisions is larger than the critical threshold distance whereby the predictions of the electron trajectory can be projected with the linear mixing rule. The simulations were subsequently performed for several incident electron energies with varying nanoparticle loadings of silica in PMMA to find the effect of nanoparticles in an electron beam resist.

5.2. Monte Carlo Simulation Procedure

In this section, a brief description of the Monte Carlo calculation procedure used for simulating electron trajectories is provided. Numerous approaches for Monte Carlo methods have been presented in literature\textsuperscript{109,110} and this work utilizes an approach similar to Murata\textsuperscript{111}. The calculation procedure described here is for a two component system consisting of a nanoparticle loaded polymer film. A simulation for a single component system of a pure polymer is performed in a similar manner assuming a weight percent
loading of nanoparticles equal to zero. The Monte Carlo simulation of electron trajectories in a two component solid target begins with the prediction of the electron step length between successive collisions. In this study, the effective density of the nanoparticle loaded polymer film is predicted according to

$$\rho_{\text{effective}} = \omega \rho_{\text{nanoparticle}} + (1-\omega) \rho_{\text{polymer}}$$  \hspace{1cm} (5.1)

where $\omega$ is the weight percent of nanoparticle in the resist, $\rho_{\text{nanoparticle}}$ is the density of the nanoparticle, and $\rho_{\text{polymer}}$ is the density of the polymer. Similarly, the mean free path of the incident electron between successive collisions is predicted according to

$$1/\lambda_{\text{effective}} = \omega/\lambda_{\text{nanoparticle}} + (1-\omega)/\lambda_{\text{polymer}}$$  \hspace{1cm} (5.2)

where $\lambda_{\text{nanoparticle}}$ and $\lambda_{\text{polymer}}$ are the mean free paths in the nanoparticle and the polymer, respectively. The total scattering cross section is the sum of the total elastic and inelastic scattering cross sections

$$\sigma_{\text{total}} = \sigma_{\text{elastic}} + \sigma_{\text{inelastic}}$$  \hspace{1cm} (5.3)

where $\sigma_{\text{elastic}}$ is calculated according to
\[ \sigma_{\text{elastic}} = (1 - \omega)\sigma_{\text{elastic, polymer}} + \omega\sigma_{\text{elastic, nanoparticle}} \]  \hspace{1cm} (5.4)

and \( \sigma_{\text{inelastic}} \) is calculated according to

\[ \sigma_{\text{inelastic}} = (1 - \omega)\sigma_{\text{inelastic, polymer}} + \omega\sigma_{\text{inelastic, nanoparticle}} \]  \hspace{1cm} (5.5)

The Monte Carlo simulation procedure for the two component system is depicted in a flowchart in Figure 5-1. A random number is generated to decide the outcome of the collisions as either elastic or inelastic depending upon the ratio of the elastic and inelastic scattering cross sections to the total scattering cross section. The next random number classifies the collision event as occurring with a nanoparticle or the polymer when compared to the nanoparticle loading in the polymer film. Once the collision event is classified as either occurring with a nanoparticle or a polymer, a standard Monte Carlo calculation procedure is followed onwards where the collision atom is chosen, energy losses are calculated, and the scattering angles for the collision event are predicted.
Introduce electron

Predict electron mean free path

Decide elastic or inelastic collision

Decide nanoparticle or polymer collision

Follow standard Monte Carlo procedure

Decide if $E < E_{\text{critical}}$

Decide if $N_{\text{simulations}} > N_{\text{desired}}$

Terminate simulations

Figure 5-1: A flowchart of the Monte Carlo simulation procedure for a two component system.
In our simulation model, the elastic scattering cross section of an atom is calculated according to Rutherford's classical equation

\[
\sigma_{i,\text{elastic}} = \frac{\pi Z_i^2 e^4}{4E^2(\mu_i(\mu_i+1))}
\] (5.6)

where \(Z_i\) is the atomic number of the atom, \(e\) is the electric charge, \(E\) is the energy of the electron, and \(\mu_i\) is the screening factor described by Nigam. Inelastic collisions were categorized as either inner shell or outer shell ionizations. The Vriens scattering cross section was used to model inner shell ionization

\[
\sigma_{i,\text{inner shell}} = \frac{\pi e^4}{E^2(1+2U_i)} \left( \frac{5}{3U_i} - 1 - \frac{2U_i}{3} + \frac{In U_i}{1+U_i} \right)
\] (5.7)

where \(U_i\) is the binding energy of the \(i\)th shell electron normalized by \(E\). For outer shell ionizations, the Moller scattering cross section was used

\[
\sigma_{i,\text{outershell}} = \frac{\pi e^4}{E^2} \left( \frac{1}{\varepsilon^2} + \frac{1}{(1-\varepsilon)^2} - \frac{1}{\varepsilon(1-\varepsilon)} \right)
\] (5.8)

where \(\varepsilon_c\) is the lower limit of energy transfer to outer shell ionizations normalized by \(E\). For these simulations \(\varepsilon_c\) was set to 0.01. The incident electron was assumed to
continuously transfer energy between successive collisions according to the Bethe's continuously slowing down approach

\[ \left( \frac{dE}{ds} \right)_{\text{Bethe}} = \frac{2\pi e^4 N Z_i}{E} \ln \left( 1 + 1.166 \frac{E}{J_i} \right) \]  

(5.9)

where \( N \) is the number of atoms per unit volume, and \( J_i \) is the ionization potential of the collision atom given by Berger-Seltzer relationship. During inelastic collisions the incident electron suffers discrete energy losses from ionization events. The discrete energy losses during an inner shell ionizations are given by

\[ \left( \frac{dE}{ds} \right)_{\text{inner shell}} = \frac{\pi e^4 N}{E(1+2U_i)} \left( \frac{2}{3} - \frac{\ln(1+U_i)}{1+U_i} \right) \]  

(5.10)

The binding energies used in this study for the various atoms simulated are listed in Table 5-1. And the discrete energy loss during outer shell ionizations are given by

\[ \left( \frac{dE}{ds} \right)_{\text{outer shell}} = \frac{\pi e^4 N}{E} \left( 2 - 3(1+U_i)(1-2U_i) + 3\ln(1+U_i) - \ln U_i \right) \]  

(5.11)

Thus the total energy loss is

\[ \frac{dE}{ds} = \left( \frac{dE}{ds} \right)_{\text{Bethe}} - \left( \frac{dE}{ds} \right)_{\text{inner shell or outer shell}} \]  

(5.12)
Table 5-1: Binding energies for orbital shells used in this work\textsuperscript{112}. All binding energies are listed in electron-volt (eV).

<table>
<thead>
<tr>
<th>Atom</th>
<th>1s</th>
<th>2s</th>
<th>2p\textsuperscript{3/2}</th>
<th>2p\textsuperscript{1/2}</th>
<th>3s</th>
<th>3p\textsuperscript{3/2}</th>
<th>3p\textsuperscript{1/2}</th>
<th>Free electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>284.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>543.1</td>
<td>41.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Carbon</td>
<td>284.2</td>
<td>30.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Silicon</td>
<td>1839</td>
<td>149.7</td>
<td>99.8</td>
<td>99.2</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Titanium</td>
<td>4966</td>
<td>560.9</td>
<td>460.2</td>
<td>453.8</td>
<td>58.7</td>
<td>32.6</td>
<td>32.6</td>
<td>5</td>
</tr>
</tbody>
</table>

In the following studies a million electron trajectories were simulated and repeated five times for each resist system. Two different studies on the consequences of high atomic number species such as silicon and titanium tagged to a PMMA molecule and nanoparticles such as silica loaded in a PMMA resist were performed. The tagging a silicon or titanium atom onto a PMMA molecule increases the density of the resist to .84 and .98 g/cm\textsuperscript{3} for the Si-PMMA and Ti-PMMA films, respectively. The density was calculated according to

\[
\rho = \nu \rho_{\text{pmma}} + (1 - \nu) \rho_{\text{metal}}
\]  \hspace{1cm} (5.13)

where \(\nu\) is the atomic fraction of PMMA in Si-PMMA and Ti-PMMA. The densities of PMMA, silicon, and titanium utilized for this work were .745, 2.33 and 4.507 g/cm\textsuperscript{3}, respectively\textsuperscript{112}. Also, the density of the silica nanoparticle used in these simulations was 2.20 g/cm\textsuperscript{3}.

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5.3. Validation of Simulations

The Monte Carlo method used in this work utilizes both Rutherford and Mott elastic scattering cross sections, Moller inelastic scattering cross section for outer shell ionizations, and Vriens inelastic scattering cross section for inner shell ionizations. The Rutherford and Mott elastic scattering cross sections were used for incident electron energies greater than and below 20 keV, respectively. Also, the energy losses were calculated according to the Bethe’s CSDA equation between collisions and through discrete energy losses during inelastic collisions. For the Monte Carlo simulations, the calculation of scattering cross sections provides the basis for most of the computations along with the energy losses calculated at the end of each collision. In order to verify the calculations made in this work, the scattering cross sections and energy losses were compared with empirical approaches published in literature.

The elastic scattering cross section was verified using an empirical form proposed by Browning for an incident electron energy range of 0.1 to 30 keV\textsuperscript{113}. In his study, Browning found that incorporating an extra energy dependent term to the Rutherford cross section resulted in excellent agreement with tabulated Mott cross section data. The proposed empirical form of the cross section was

\[
\sigma = \frac{4.7 \times 10^{-18} (Z^{1.33} + 0.032Z^2)}{(E + 0.155Z^{1.33} E^{-5}) (1 - 0.02Z^{-0.05} \exp(-u^2))} \tag{5.14}
\]

where
\[ u = \log_{10}(8EZ^{-1.33}) \]  

(5.15)

and \( Z \) and \( E \) are the atomic number and energy, respectively. This empirical equation was compared to the elastic scattering cross sections calculated in this work using Rutherford cross section for silicon and titanium in Figure 5-2 and Figure 5-3, respectively. It can be observed that the calculations used in our simulations matched very closely to the empirical cross section suggested by Browning. Further, as expected the elastic scattering cross section for titanium is greater than silicon as a consequence of a higher atomic number.

![Graph showing comparison of total elastic scattering cross section calculated in this work and Browning's empirical equation for a silicon atom.](image)

**Figure 5-2:** Comparison of total elastic scattering cross section calculated in this work and Browning’s empirical equation for a silicon atom.
The inelastic scattering cross section was verified using the classical description of bound electrons in the various electronic shells as free electrons. All the electrons bound to the atom are treated similarly instead of classifying them as bound electrons for shells which are fully occupied and the last partially occupied shell as a free electron shell. This classical cross section is given by

$$\sigma = \pi a_0^2 \left( \frac{e^2}{a_0} \right)^2 \left[ \frac{1}{\varepsilon_c^2} + \frac{1}{(1-\varepsilon_c)^2} \right]$$  \hspace{1cm} (5.16)
where $\varepsilon_c$ is the minimal value for energy transfer. The value of $\varepsilon_c$ was chosen to be 0.01 below which no significant change in the energy distribution was found. Figure 5-4 and Figure 5-5 plot the comparison between the inelastic scattering cross section calculated in the present work with that of the classical equation for silicon and titanium, respectively. In the present work, inelastic scattering cross section was classified according to inner shell and outer shell ionizations and calculated for each electronic shell. Due to the approximation of inner shell bound electrons as free electrons, the classical cross section predicts a larger inelastic cross section for both silicon and titanium. Above 10 keV incident electron energy, the classical equation and the calculation used in the present work are in good agreement. Also, Figure 5-6 and Figure 5-7 plot the individual electronic shell contributions to the inelastic scattering cross sections of silicon and titanium. It can be observed that the contribution to the scattering cross section increases as the shell electron becomes less bound to the atom. The major contribution is from the free electron shell followed by the 3s, 2p, 2s, and 1s shells. The tightly bound 1s and 2s electrons contribute minimally to the scattering cross section.
Figure 5-4: Comparison of total inelastic scattering cross section calculated in this work and the classical approach for a silicon atom.

Figure 5-5: Comparison of total inelastic scattering cross section calculated in this work and the classical approach for a titanium atom.
Figure 5-6: A plot of total inelastic scattering cross section contributions from the various subshells of a silicon atom.

Figure 5-7: A plot of total inelastic scattering cross section contributions from the various subshells of a titanium atom.
Finally, the energy losses were verified using Joy and Luo’s empirical equation that accounts for both elastic and inelastic energy losses during the electron trajectory. This approximation eliminates the necessity of formulating energy losses for different kinds of discrete energy losses such as free electron ionizations and inner shell ionizations. The approximation is given by

\[
\frac{dE}{ds} = 785 \frac{\rho Z_i}{AE} \ln \left( 1.166 \frac{E + t J_i}{J_i} \right) \quad (5.17)
\]

where \( t \) is a variable whose value depends on the atom and is always close to but less than unity. Figure 5-8 and Figure 5-9 compare the approximation to Bethe’s CSDA approach used in this simulation for carbon and oxygen. Both approaches of calculating the energy loss in these simulations are in close agreement.
Figure 5-8: Comparison of energy losses calculated in this work and the Joy and Luo’s empirical equation for a carbon atom.

Figure 5-9: Comparison of energy losses calculated in this work and the Joy and Luo’s empirical equation for an oxygen atom.
The validation of the Monte Carlo simulation has been illustrated by comparing the calculation of elastic scattering cross section, inelastic scattering cross section, and energy losses with empirical formulae developed in literature. The elastic scattering cross section calculated in this work was compared to the empirical Browning formula and found to be in excellent agreement. The inelastic scattering cross section was compared with the classical Moeller equation and found to be more accurate since the Moeller equation does not distinguish between inner shell and outer shell electrons. The inelastic scattering cross section was calculated for each of the electronic shells in the atom that improves the accuracy of the simulations. Finally, the calculation of the energy losses suffered by the traversing electron was found to be in excellent agreement with the Joy and Luo equation. These confirmations validate the simulations performed in the following chapters for studying the effects of high atomic number species and nanoparticles loaded in an electron beam resist.

5.4. Results and Discussion

5.4.1. Effects of high atomic number species

5.4.1.1. Effects of film densification

The density of a resist material primarily determines the mean free path and in consequence the number of collisions that an incident electron encounters in its trajectory through the resist. Also, the difference in density between the resist and the substrate
material underneath determines the backscattering coefficient at the interface. With a higher density material, an incident electron will suffer a greater number of collisions with the various atoms in its flight through the resist as a consequence of decreased mean free path. This material density effect can be studied by increasing or decreasing the number of atoms in a constant unit volume in order to increase or decrease the density, respectively. Here we investigated the effects of changing the number of atoms in a constant unit volume of a PMMA resist film. This simulation would hypothetically imitate a situation where no molecular changes occurs between an organic and an inorganic resist, except that the density is either increased or decreased. Therefore, we can uniquely understand the effects of material density on the interaction with incident electrons. A dimensionless density is introduced which is the ratio of the density of the hypothetical PMMA film to that of a standard PMMA film \( \rho_{\text{dimensionless}} = \rho / \rho_{\text{PMMA}} \). The following dimensionless densities were investigated: .25, .5, 1, 2, and 4. In the case study of the dimensionless density equaling 1, the simulation is of a standard PMMA film. For the dimensionless density of 4, the simulation occurs on a hypothetical PMMA film with 4 times the density of a standard PMMA film. Similarly, for the dimensionless density of .25, the simulation occurs on a hypothetical PMMA film that is \( \frac{1}{4} \)th of the density of a standard PMMA film.

As expected, the mean free path of an incident electron decreases with increasing dimensionless density which implies an increasing number of collisions suffered by incident electrons. Figure 5-10 shows the average radial distance that an incident electron traveled between collisions in its trajectory through a 500 nm resist film at three different accelerating potentials (10, 25, and 50 keV). For each accelerating voltage and
dimensionless density, five repeats of 500000 electron trajectories were performed to obtain statistically meaningful values. Typically, a density of an inorganic film would correspond to a dimensionless density between 1 and 2 on the abscissa. In this regime, the average radial distance traveled between successive collisions by an incident electron is reduced by about 20% for all different accelerating voltages simulated. However, with increasing dimensionless density, the average distance traveled by an incident electron into the depth of the film also decreases. When an incident electron interacts with a high density material, the average radial distance and average depth distance traveled between successive collisions both decrease. With a higher density material, the beam broadening in the top portion of the film can be narrower as compared to a lower density material because the average radial distance traveled between collision events is smaller. Hence, there exits a cutoff depth above which a high density material provides better resolution than a low density material. This cutoff depth is dependent upon the material density, atomic constituents of the material, and accelerating voltage.
5.4.1.2. Collisional statistics

The consequences of adding high atomic number species to an electron beam resist on collisional statistics was studied by tagging a silicon or a titanium atom onto a PMMA molecule. Electron trajectories were monitored in a 200 nm thick freestanding film for incident electron energies of 25, 50, 75, and 100 keV. The number of elastic and inelastic collisions for each incident electron was recorded and averaged with the total...
number of simulated electrons. A plot of the ratio of elastic to inelastic collisions per incident electron for the various films and incident electron energies is shown in Figure 5-11. For all the films the ratio is approximately constant over the range of incident electron energies investigated. This would be expected as the inelastic collision probability will generally tend to increase for incident electron energies below about 10 keV. It can be observed that the ratio increases with the inclusion of high atomic number species. The ratio for a PMMA film is about 3.09 while it increases to approximately 3.93 and 5.21 for silicon and titanium tagged PMMA films at 50 keV, respectively. The increase can be attributed to the nuclei of the high atomic number species which provides a higher charge resulting in a stronger shielding of the atom and enhancement of elastic collision probability for impinging electrons. Therefore, elastic collisional processes are more favored in a resist system containing high atomic number species along with an increased number of collisions due to an increasing density of the solid target.
A stronger shielding force caused by the high atomic number species also results in a larger deflection angle of the incident electrons undergoing elastic collisions with the high atomic number species. Figure 5-12 compares the average elastic scattering angle suffered by incident electrons in their trajectory through the three films at various incident electron energies. As expected the deflection angle of incident electrons increases with progressively increasing shielding force from PMMA, Si-PMMA, to Ti-PMMA. For PMMA the average elastic scattering angle decreases from $2.52^\circ$ to $1.52^\circ$ between 25 and 100 keV incident electron energies. Similarly, the average elastic scattering angle decreases from $3.78^\circ$ to $2.15^\circ$ and $3.97^\circ$ to $2.25^\circ$ for Si-PMMA and Ti-PMMA, respectively, between 25 to 100 keV incident electron energies. Due to a decreasing screening factor with increasing incident electron energy a decrease in the

**Figure 5-11:** Ratio of elastic to inelastic collisions per incident electron at several incident electron energies for the different films.
average elastic scattering angle is observed. Also, the average inelastic scattering angle was not affected by inclusion of the high atomic number species since the interaction is that of an electron colliding with another electron which becomes indistinguishable for the different atomic species as illustrated in Figure 5-13. The average inelastic scattering angle was found to be about 7.84°, 7.67°, and 7.45° for PMMA, Si-PMMA, and Ti-PMMA, respectively, for the different incident electron energies. Thus, the inclusion of high atomic number atoms increases the ratio of elastic to inelastic collisions per incident electron and the average elastic scattering angle suffered by an incident electron while the average inelastic scattering angle remains unchanged.

**Figure 5-12:** Average elastic scattering angle at several incident electron energies for the different films.
5.4.1.3. Dimensionless electron trajectory and point electron distributions

The number of collisions suffered by an impinging electron is proportional to the density of the film which increases with the atomic number of the tagged species. With increasing density the incident electron becomes more constrained in its trajectory through the film as the average mean free path is reduced. Here, the average radial distance and depth distance traveled between successive collisions were monitored for various incident electron energies in the different films. Figure 5-14 plots the dimensionless ratio of the average depth distance and average radial distance traveled between successive collisions which defines the resolution attainable in a resist. A high ratio represents a nearly straight line trajectory while a low ratio represents a trajectory
strongly diverging from the straight line path. The dimensionless ratio increases with incident electron energy for all films as higher energy electrons obtain higher directionality due to smaller scattering angles. At 25 keV incident electron energy, the dimensionless ratio decreases from 8.26, 6.22, to 4.43 for PMMA, Si-PMMA, and Ti-PMMA, respectively. Thus addition of high atomic number species reduces the resolution at this incident electron energy. At 50 keV incident electron energy, the dimensionless ratio of Si-PMMA becomes comparable with PMMA while the difference between PMMA and Ti-PMMA is reduced. At higher incident electron energies, the dimensionless ratio of Si-PMMA and Ti-PMMA both exceed that of PMMA. At 75 keV incident electron energy, Si-PMMA and Ti-PMMA exhibit dimensionless ratios of 18.83 and 17.62, respectively, compared to a ratio 17.84 for PMMA. At 100 keV incident electron energy the ratio of Ti-PMMA also exceeds PMMA. The increase in the dimensionless ratio is a consequence of increased film density where the average radial distance traveled between collisions is reduced as the impinging electrons becomes radially constrained in their trajectory. At these high incident electron energies the higher density films are able to constrain the incident electrons to smaller radial distances traveled between collisions while maintaining their high directionality resulting in larger dimensionless ratios. With low incident electron energies, the impinging electron directionality is too small to take advantage of the radial containment. Finally, it should be noted that the dimensionless ratio is dependent upon film thickness and that it should be calculated for thicknesses where the point electron distribution for different films is of interest.
Figure 5-14: Dimensionless ratio of average depth distance to average radial distance traveled between successive collisions in the different films at various incident electron energies.

The point electron distributions for the three films were also monitored at several incident electron energies. As a consequence of increased density with high atomic number species, incident electrons have a shorter mean free path between successive collisions and consequently suffer a larger number of collisions during their trajectory through the film. It was previously found that the dimensionless electron trajectory for Si-PMMA and Ti-PMMA exceeded PMMA for high incident electron energies. In this study the average radial position of incident electron trajectories were monitored at 50 nm intervals into the depth of the film. Figure 5-15 plots the difference in average radial position between high atomic number species containing films and PMMA. At 25 keV incident electron energy, the difference in average radial position at a depth of 200 nm is
about 8.02 and 23.05 nm for Si-PMMA and Ti-PMMA, respectively. At 50 keV incident electron energy, the differences between Si-PMMA and PMMA becomes negligible while Ti-PMMA yet has a slightly larger point electron spread than PMMA. At incident electron energies greater than 50 keV, both Si-PMMA and Ti-PMMA exhibited smaller point electron spreads as compared to PMMA. At a film depth of 200 nm, a difference of -0.79 and -0.94 nm was observed at 75 and 100 keV incident electron energy, respectively for Si-PMMA. Similarly, the difference was about -0.32 and -0.83 nm for Ti-PMMA at these high incident electron energies. As previously mentioned, the higher density films are able to radially constrain the incident electrons resulting in a narrower point electron distribution between the high atomic number species film and organic resist at high incident electron energies. Thus a method of obtaining better resolution than organic resists with high atomic number species resists is through the use of high incident electron energies with a high density film with a thickness of about 200 nm.
Figure 5-15: Differences in point electron spreads between a PMMA film (a) Si-PMMA and (b) Ti-PMMA at various incident electron energies.
5.4.2. Effects of nanoparticles

5.4.2.1. Nanoparticle collision probability

The distribution of nanoparticles in a polymer film can be assumed to be homogenous and random at low loadings such that coagulation is not observed. While simulating the impact of nanoparticles on incident electron trajectories, an assumption which can be made in the Monte Carlo calculation procedure is to assign the collision probability between nanoparticles and incident electrons to be equivalent to the weight percent loading of the nanoparticles in the film. In order to verify the assumption, a thousand electron trajectories were recorded in a 500 nm thick PMMA film for various incident electron energies ranging from 10 to 100 keV and tracked through a randomly assigned three dimensional lattice representing a silica nanoparticle loaded PMMA film. Each site in the three dimensional lattice is assigned to represent a nanoparticle or a polymer according to the weight percent loading of nanoparticles in the polymer film. Also, the size of the lattice was chosen to represent the typical size of a nanoparticle dimension which is on the order of a nanometer. Each collision event was counted as either a nanoparticle or polymer collision depending upon whether the collision event occurred inside a lattice site containing a nanoparticle or polymer, respectively. The nanoparticle loadings studied ranged from 0 to 0.1 and 0.1 to 1 with 0.01 and 0.1 increments, respectively. For each nanoparticle loading ten repeats were performed and an average value of the observed collision probability is reported. It was found that the differences between observed and assigned nanoparticle collision probabilities were
negligible for a large range of incident electron energies between 10 and 100 keV as shown in Figure 5-16. In this figure the observed nanoparticle collision probabilities are plotted for 2, 4, and 8 wt% loading of nanoparticles in the polymer film for 10 keV incident electron energy increments from 10 to 100 keV. Therefore, it was assumed that the collision probability between incident electrons and the nanoparticles could be assigned to be equal to the loading of nanoparticles in the polymer film in the range of incident electron energies investigated in this percolation study.

Figure 5-16: A plot of observed nanoparticle collision probability at various incident electron energies.
5.4.2.2. Effective film properties

In order to perform a Monte Carlo calculation, isotropic film properties are required to predict the electron trajectory through the film and layers beneath. For a nanoparticle loaded film the properties are anisotropic near the location of the nanoparticle and tend towards isotropic values for large distances away from the nanoparticle. In order to determine the transition from anisotropic to isotropic film behavior a three dimensional site percolation study was performed where each site was randomly assigned as a nanoparticle or a polymer depending upon the loading of the nanoparticles in the film. Using this site percolative approach, random sites could be selected to study the changes in film properties from local to global behavior. If a transition from anisotropic to isotropic behavior exists, it can be calculated for various nanoparticle loadings and a critical distance can be estimated from the reference site at which properties could be estimated from a linear mixing rule. Therefore, the criteria for a valid simulation will be to require that the average mean free path between successive collisions of the electron trajectory to be greater than the critical threshold. That is, a fast traveling electron is assumed to experience the effective film properties estimated from the individual polymer and nanoparticle properties.

The cubic lattice consisted of one thousand sites to each side and the site length was chosen to be a nanometer which is a typical size of a nanoparticle. Next, each site in the lattice was randomly assigned the density value of the nanoparticle or polymer by comparing a random number with the percentage of nanoparticles loaded in the resist. Subsequent to percolative buildup, a random lattice site was selected and the effective
density was calculated for desired lattice sites away from the reference site by summing the density values of the lattice sites and dividing by the number of lattice sites sampled. The density was sampled up to 200 site lengths and hence, the reference site was chosen such that it was located a minimum of 200 sites away from each boundary. The effective density was averaged over 1000 electron locations chosen randomly for each nanoparticle loading. A plot comparing the difference between the calculated and predicted density is shown in Figure 5-17 for a 2, 4, and 8 wt% nanoparticle loading in the film. It can be seen that fluctuations in density decay with increasing step lengths and converge to a global value predicted through the linear mixing rule. Further, fluctuations for different nanoparticle loadings were also observed to terminate beyond 4-5 step lengths relative to the reference site. Hence, for the purpose of this simulation, isotropy of material properties can be assumed for predictions on the size scale greater about 5 step lengths. Therefore, if an average mean free path of an incident electron is greater than about 5 nm in its trajectory through a film, its flight can be assumed to be altered by the effective properties predicted by the linear mixing rule. Similarly, other properties such as elastic and inelastic scattering cross sections show similar trends of obeying the linear mixing rule beyond the critical step length of 4 to 5 sites.
5.4.2.3. Point electron distributions

The point electron distribution was monitored for 2, 4, 6, 8, and 10 wt% silica loadings in PMMA for incident electron energies of 25, 50, 75, and 100 keV. The average radial location of incident electrons was monitored at each 50 nm interval into the depth of the film. Figure 5-18 and Figure 5-19 plot the difference in point electron distributions as compared to a film without nanoparticles for the various incident electron energies. At 25 and 50 keV incident electron energies, the point electron distributions are...
slightly larger. At a depth of 200 nm, the difference is about 1.14 and 0.26 nm for a nanoparticle loading of 10 wt% for 25 and 50 keV incident electron energies, respectively. The differences in the point electron spreads have been approximately reduced by a factor of two for all nanoparticle loadings as the incident electron energy is increased from 25 to 50 keV. The increased effective film density experienced by the incident electron decreases the mean free path between successive collisions and henceforth the incident electron continuously spreads more radially with increasing nanoparticle loading. For higher incident electron energies of 75 and 100 keV, the differences are almost negligible for all nanoparticle loadings. This result is similar to the observations made with high atomic number species containing films. With increasing nanoparticle loadings the film gets denser whereby constraining the motion of incident electrons through the film. At high incident electron energies this radial constraint from increased nanoparticle loadings provides point electron distributions comparable to a film without nanoparticles.
Figure 5-18: Differences in point electron spreads between a PMMA film and for various nanoparticle loadings at incident electron energies of (a) 25 keV and (b) 50 keV.
Figure 5-19: Differences in point electron spreads between a PMMA film and for various nanoparticle loadings at incident electron energies of (a) 75 keV and (b) 100 keV.
5.5. Summary and Conclusions

The consequences of high atomic number species and nanoparticles in an electron beam resist have been studied. With high atomic number species in a resist, stronger shielding of the atom due to a highly charged nuclei results in a larger average elastic scattering angle while the average inelastic scattering angle does not change since the interaction is between the incident electron and the orbital electron which is invariant with the different atoms. The introduction of high atomic number species increases the density of the film resulting in a reduced mean free path for impinging electrons. It was found that the radial containment of incident electrons with higher density films could be taken advantage of with high incident electron energies. The point electron distributions at incident electron energies greater than 50 keV were found to be comparable or better for Si-PMMA and Ti-PMMA as compared to PMMA. A similar effect was observed for nanoparticles loaded in a resist where the effective density of the film increases with higher nanoparticle loadings. As a consequence of densification, the point electron spreads were found to comparable to a film without nanoparticles at high incident electron energies of 75 and 100 keV with varying nanoparticle loadings from 2 to 10 wt%.

In general, the addition of high atomic number species and nanoparticles in an electron beam resist could be used to enhance the resolution as compared to an organic resist. In order to obtain comparable resolution of an organic resist, a very thin film combined with high incident electron energy is required. With these conditions, the incident electron is radially constrained and provides higher resolution as compared to
organic resists. Another possible regime of achieving similar performance to an organic resist is through the use of very low incident electron energies. In this regime, the incident electrons are much more likely to undergo inelastic scattering events where the nature of the scattering atom becomes irrelevant. For moderate incident electron energies, the point electron spread is larger in a high atomic number species and nanoparticle containing films as compared to an organic resist.
CHAPTER 6

6. ELECTRON BEAM PATTERNING OF SELF ASSEMBLED MONOLAYERS: A MONTE CARLO INVESTIGATION

6.1. Introduction

As semiconductor devices are progressively miniaturized in accordance with Moore’s law, alternative resists materials and patterning methods are continuously explored for future lithographic generations of semiconductor device manufacturing. Traditionally, resist materials have been developed to respond upon exposure to light through the generation of an acid which is used to amplify the necessary transitions required within the resist for pattern delineation. With optical lithographic patterning of semiconductor devices, miniaturization of critical dimensions has been primarily brought about through reductions in the wavelength of light used to expose photoresists\textsuperscript{114}. However, reductions in the wavelength of light have necessitated tailoring of resist materials with absorption properties attenuated for the desired wavelength of exposure\textsuperscript{115,116,117}. This progressive transition to smaller exposure wavelengths in the deep ultraviolet region has narrowed the possibility of finding suitable resist and optical lens materials and has necessitated alternative approaches beyond optical lithography\textsuperscript{118,119}.
An alternative approach to optical lithography that has been considered for the past two decades in semiconductor device manufacturing has been electron beam lithography\textsuperscript{120}. It offers excellent resolution since the wavelength of electrons is on the order of Angstroms but it has been seldom utilized due to its inherently low throughput pixel-to-pixel exposure limitation\textsuperscript{121}. However, recent progress has been made in advancing the technology to a projection based method that drastically improves throughput\textsuperscript{122,123}. Thus, with these developments in projection electron beam lithography tools new processes and electron beam resist materials are being explored. Typically, electron beam patterning is achieved with resist film thicknesses between 200 to 500 nm at moderate incident electron energies around 10 to 40 keV. For such electron beam exposures the attainable resolution is restricted by the radial spread of the primary electron beam within the resist film prior to entering the layers beneath. In order to improve resolution, the resist film thickness can been decreased while simultaneously increasing the incident electron energy to confine the radial spread of the electron beam by ensuring that incident electrons follow a nearly straight line trajectory through the film\textsuperscript{124,125}. An ultimate extension of this thin film patterning approach is the use of self assembled monolayers (SAMs) which are coated through an immersion process and are strongly bound to the substrate with a thickness of a few nanometers\textsuperscript{126,127,128,129,130}. Upon electron beam bombardment and possible post-treatment, the monolayer can either be decomposed or chemically modified in such a way that it can be subsequently used to provide etch contrast for defining patterns using conventional plasma or wet etching methods. For example, the monolayer may contain reactive functional groups that can serve as radical initiators for graft polymerization of polymer onto the surface\textsuperscript{131}. By
exposing such a monolayer to electron beam radiation, the radical initiator sites in the monolayer could be deactivated, such that post-exposure polymerization using the monolayer only results in polymer formation in the unexposed areas of the SAM. The grown polymer patterns can then serve as protective etch masks for further processing. Similar strategies can be employed where the exposed and patterned SAM is functionalized by the addition of metal to also produce patterned etch masks. However, if such monolayer based methods are to be used with electron beam lithography, some basic understanding of the interaction of the electron beam with the monolayer would be useful in understanding the limitations and characteristics of such processes.

The transfer of energy during electron beam bombardment of the monolayer can be achieved through: (1) forward scattering where the primary electrons could collide elastically or inelastically with the atoms while continuously depositing energy within the monolayer, (2) secondary electrons generated within the monolayer or near the monolayer/substrate interface, or (3) backscattered electrons from the substrate. Ideally, the highest resolution would be achieved if the energy transfer occurred solely through forward scattering where the point electron spread is minimized due to the relatively small thickness of the monolayer. The resolution would be degraded by the generation of secondary electrons and backscattered electrons that can traverse in random directions and transform the monolayer in undesired locations. In this process, almost all incident electron trajectories will be transmitted into the substrate since the typical thickness of a monolayer is on the order of 1.5 – 2 nm which is the typical mean free path of a low energy secondary electron. Therefore, the energy transferred to the monolayer through
backscattering from the substrate and secondary electrons generated near the monolayer/substrate interface will determine the resolution attainable using this patterning approach. Additionally, generation of secondary electrons within the monolayer is minimal as the incident electron trajectories are mostly transmitted to the substrate without colliding with the atoms contained in the monolayer. Also, the probability of secondary electrons generated near the monolayer/substrate interface and obtaining the directionality to reach and interact with the monolayer is minimal. Thus, backscattered electrons from the substrate could determine the resolution attainable in this ultrathin film monolayer imaging approach.

In this study, Monte Carlo simulations are employed to study the process of electron beam transformation of a self assembled monolayer. A 2 nm thick poly(methyl methacrylate) PMMA film on top of an infinitely thick silicon substrate was used to represent the process. Electron trajectories were monitored for various incident electron energies to determine the effects of forward and backward scattering electrons on the resolution attainable with the process. In order to understand the consequences of backscattered electrons, their radial spreads and depth distributions were monitored and correlated. Also, backscattered electrons were classified according to the number of large angle scattering events suffered and characteristic backscattering events were classified for various energies. Finally, the energy dissipated in the monolayer through forward scattering and backscattering electrons was studied.
6.2. Monte Carlo Simulation Procedure

The Monte Carlo method for simulating electron trajectories in a solid medium is widely utilized and numerous approaches have been previously reported in literature\textsuperscript{133,134,135}. After impinging a solid medium, an electron is deflected upon elastically or inelastically colliding with atoms in its trajectory while continuously transferring energy to its surroundings between successive collisions. In this work, the elastic scattering cross section was calculated using Mott’s equation expressed by

\[
\frac{d\sigma}{d\Omega} = \left| f(\theta) \right|^2 + \left| g(\theta) \right|^2
\]  

(6.1)

where the functions \( f(\theta) \) and \( g(\theta) \) are the scattering amplitudes given by

\[
f(\theta) = \frac{1}{2iK} \sum_{l=0}^\infty \left\{ (l+1) \{ \exp(2i\delta_l) - 1 \} + \sum_{m=0}^{l-1} \exp(2i\delta_{l-m}) \} \right\} P_l \cos \theta
\]  

(6.2)

\[
g(\theta) = \frac{1}{2iK} \sum_{l=0}^\infty \left\{ -\exp(2i\delta_l) + \sum_{m=0}^{l-1} \exp(2i\delta_{l-m}) \right\} P^l_1 \cos \theta
\]  

(6.3)

where \( K \) is the wave number of the electron, \( P_l \) and \( P^l_1 \) are the Legendre function and the associated Legendre function, respectively, and \( \delta_l \) is the phase shift of the \( l \)th partial wave. Tabulated Mott differential scattering cross section data consisting of 1\(^\circ\) increments up to 10\(^\circ\) and 2\(^\circ\) increments until 180\(^\circ\) for 25, 50, 75, 100, 200, …, 1000,
2000, ..., 10000, 15000, ..., and 30000 eV electron energies were utilized. During the simulations, a linear interpolation was performed to estimate the differential scattering cross section for a traversing electron energy. Inelastic collisions were categorized as either inner shell or free electron outer shell ionizations. The Vriens differential scattering cross section for the $i$th inner shell is given by

$$
\left[ \frac{d\sigma}{d\varepsilon} \right]_{\text{inner shell}} = \frac{\pi \varepsilon^4}{E^2(1+2U_i)} \left\{ \frac{1}{\varepsilon^2} + \frac{4U_i}{3\varepsilon^3} + \frac{1}{(1+U_i-\varepsilon)^2} + \frac{4U_i}{3(1+U_i-\varepsilon)^3} \right\}
$$

where $U_i$ and $R_y$ are the binding energy of the $i$th shell electron normalized by $E$ and the Rydberg energy normalized by $E$, respectively. And the Møller cross section, derived assuming atomic electrons as free electrons, is used to predict outer shell ionization according to

$$
\left[ \frac{d\sigma}{d\varepsilon} \right]_{\text{outer shell}} = \frac{\pi \varepsilon^4}{E^2} \left\{ \frac{1}{\varepsilon^2} + \frac{1}{(1-\varepsilon)^2} - \frac{1}{\varepsilon(1-\varepsilon)} \right\}
$$

where $\varepsilon$ is the energy transferred to the secondary electron normalized by the energy of the primary electron. Since atomic electrons are assumed to be free, $U_i = 0$, and
assuming \( R_z = 0 \), the Vriens cross section reduces to the Moller cross section. The binding energies and the number of free electrons used for the various atoms in these simulations are listed in Table 6-1.

### Table 6-1: Binding energies (eV) of electronic shells used in this work.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electronic shell</th>
<th>1s</th>
<th>2s</th>
<th>2p(_{1/2})</th>
<th>2p(_{3/2})</th>
<th>free electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td></td>
<td>284.2</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td>284.2</td>
<td>30.3</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td>543.1</td>
<td>41.6</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>1839</td>
<td>149.7</td>
<td>99.8</td>
<td>99.2</td>
<td>4</td>
</tr>
</tbody>
</table>

Upon impinging a solid target, the electron step length \( s \) is calculated according to

\[
R_1 = 1 - \exp\left(-s/\lambda_m\right)
\]

(6.6)

where \( \lambda_m \) is the mean free path of the electron given by
\[ 1/\lambda_m = 1/\lambda_{\text{elastic}} + 1/\lambda_{\text{inelastic}} \]  

The elastic and inelastic mean free paths are determined by the atomic constituents and the density of the material according to

\[ \frac{1}{\lambda_{\text{elastic}}} = N_A \rho \sum_i \frac{w_i \sigma_{\text{elastic},i}}{A_i} \]  
\[ \frac{1}{\lambda_{\text{inelastic}}} = N_A \rho \sum_i \frac{w_i \sigma_{\text{inelastic},i}}{A_i} \]  

where \( N_A \) is Avogadro’s constant, \( \rho \) is the density, \( w_i \) is the weight fraction of the atom \( i \), \( A_i \) is the molecular weight of the atom \( i \), \( \sigma_{\text{elastic},i} \) is the total elastic scattering cross section of the atom \( i \), and \( \sigma_{\text{inelastic},i} \) is the total inelastic scattering cross section of the atom \( i \). The primary electron is assumed to continuously transfer energy to the solid target between successive collisions according to Bethe’s equation

\[ \left( \frac{dE}{ds} \right) = \frac{2 \pi e^4 N Z_i}{E} \ln \left( 1 + \frac{1.166 E}{J_i} \right) \]  

where \( Z_i \) is the atomic number and \( J_i \) is the ionization potential of the collision atom given by the Berger-Seltzer relationship

\[ J_i = 9.76 Z_i + 58.8 Z_i^{-.19}. \]

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Besides continuously losing energy during the trajectory through the solid, the electron also transfers energy to the medium during inelastic collisions. When a free electron collision occurs, the energy loss is given by

\[
\left( \frac{dE}{ds} \right)_{\text{outer shell}} = \frac{\pi e^4 N}{E} \left( 2 - 3 \ln 2 - \frac{1}{1 - \varepsilon_c} - 2 \ln(1 - \varepsilon_c) - \ln \varepsilon_c \right) \]

(6.11)

where \( \varepsilon_c \) the lower limit of energy transfer to free electron collisions normalized by \( E \).

In these simulations the lower limit of energy transfer was set to 0.01. Finally, the energy loss during an inner shell ionization is given by

\[
\left( \frac{dE}{ds} \right)_{\text{inner shell}} = \frac{\pi e^4 N}{E(1 + 2U_i)} \left( \frac{2}{3} - 3 \ln 2 + \frac{1}{3} (1 + U_i)(1 - 2U_i) + 3 \ln(1 + U_i) - \ln U_i \right). \]

(6.12)

During the Monte Carlo simulation, changes in material properties used to predict the trajectory as electrons traverse from one layer to another is typically ignored for simplicity and ease of calculation. Using this assumption, where the average mean free path of an electron is much smaller than any of the film thicknesses in the stack, introduces minimal error into the predictions. However, this assumption should not be used for very thin films or high incident electron energies where the predicted electron trajectory could enter large distances into a new layer for which the material properties are different from the originating layer. Due to the relatively small thickness of the monolayer, simulations should account for the change in material properties when an electron crosses an interface in order to accurately predict the electron trajectories.
Different approaches have been proposed for adjusting the predicted trajectory whenever an interface is crossed and are shown in Figure 6-1. Suppose that the mean free paths of an electron in two different layers are $\lambda_1$ and $\lambda_2$ and that the electron has crossed the interface with predictions based upon the material properties of the 1st layer. A method proposed by Hen$^{136}$ predicted the mean free path using $s_1/\lambda_1 + s_2/\lambda_2$ where $s_1$ and $s_2$ are the distances traversed by the electron in each layer. If the newly predicted mean free path crosses the interface the move is accepted, otherwise, the procedure is repeated until the electron mean free path crosses the interface. This model behaves well when $s_1$ and $s_2$ are approximately equivalent but the predictions become less accurate when $s_2 >> s_1$ or $s_1 >> s_2$. Also, Lu$^{137}$ published a refraction type model where the mean free paths of the interface crossing electron is predicted assuming the material properties of both layers and a new location in the second layer is determined. In this method, step lengths $s_1$ and $s_2$ and scattering angles $\theta_1$ and $\theta_2$ are calculated for each of the layers at the location where the electron incurred a collision prior to crossing the interface. Next, a balance is performed to calculate the length traveled in the new layer according to the summation of scattering fractional lengths in each layer. Finally, the refraction angle is assumed to be the difference between the previously predicted scattering angles ($\Delta \theta = \theta_1 - \theta_2$). In this work, a more accurate representation of the process has been adopted where the electron trajectory crossing two different layers is traced back to the interface and the next collision event is predicted with properties of the new layer. As the electron is traced back to the interface the locations and the energy are reinitialized according to the distance traversed in the originating layer. This procedure requires more
calculations but provides a more accurate simulation for ultrathin films such as self-assembled monolayers that are the subject of this work.

Figure 6-1: A summary of different methods used while an interface is crossed during an electron trajectory: (a) Han’s method of linear correlation, (b) Lu’s method of electron refraction, and (c) Method used in this work where the electron is traced back to the interface.
6.3. Results and Discussion

6.3.1. Collision probability

In a standard electron beam lithography process incident electrons typically suffer numerous collisions within the resist prior to entering the layers beneath. In between successive collisions energy is continuously transferred to the resist as the electron is slowed down by the solid target. Also, secondary electrons generated from inelastic collisions could further cause a cascading process of knock on electrons. Contrastingly, high resolution electron beam lithography requires utilization of high energies where the incident electrons suffer few collisions with the medium and maintain a nearly straight line trajectory through the resist. Therefore, a higher electron beam dose is required to initiate dissolution modulation events in the resist since the number of interactions between the incident electrons and the atoms are minimized. With the ultrathin film monolayer imaging approach, incident electrons are likely to be transmitted to the silicon substrate without suffering any collisions with the monolayer whereby drastically increasing the electron beam dose required to pattern these materials. However, the required electron beam dose could be reduced through the use of low incident electron energies where the interaction between the incident electrons and the monolayer is increased. In this section, the interaction between incident electrons and the monolayer have been studied for various energies to understand the collisional characteristics during electron beam bombardment of the monolayer.
Figure 6-2 plots the average number of elastic and inelastic collisions per incident electron along with their sum for various energies. The monitored collisions include both forward and backward scattering electrons. It can be observed that for energies greater than 10 keV, the average number of collisions per incident electron is almost zero. At these incident electron energies most primary electrons escape and deposit in the silicon substrate without interacting with the monolayer. As the energy is decreased, the average number of elastic and inelastic collisions per incident electron begin to increase exponentially. These incident electrons show a propensity of directly interacting with the monolayer during their electron trajectory whereby the electron beam dose to print these materials will be lowered as a consequence. At 1, 2, 4, 6, and 8 keV incident electron energies, the average number of collisions per incident electron is 0.70, 0.30, 0.12, 0.07, and 0.04, respectively. At and above 4 keV incident electron energies, the ratio of elastic to inelastic collisions per incident electron is approximately 3. At incident electron energies of 1 and 2 keV, the ratio increases to 0.88 and 1.45, respectively, since decreasing the incident electron energy increases the inelastic collision probability where the electron interacts with the electron cloud surrounding the atom. Further, these results indicate that the throughput of a SAM process would be expected to behave exponentially depending upon the incident electron energy. That is, an exponential dependence of energy deposition is expected where lower energies should be utilized for high throughput.
6.3.2. Backscattered radial and depth distributions

With this ultrathin film monolayer imaging approach, the forward scattering spread is minimized and the primary resolution limiting mechanism could be backscattered electrons from the substrate. The fraction of the electron trajectories that are backscattered from the substrate into regions far away from the entrance of the point electron beam where electron energy transfer is undesired restricts the resolution attainable using the self-assembled monolayer ultrathin resist approach. In order to study
the backscattered electron distributions, electron trajectories of a point source electron beam incident on a monolayer on a infinitely thick silicon substrate were monitored until the incident electron backscattered into vacuum or when the energy of the traversing electron fell below a threshold energy of 100 eV. The radial distribution of backscattered electrons was collected in a radial bin size of one nanometer and normalized by the total number of backscattered electrons for each incident electron energy. Figure 6-3 and Figure 6-4 plot the normalized backscattered radial electron distributions for various energies. With increasing energies the distributions become broader as the point electron spread broadens within the silicon substrate and the fraction of the electrons that are backscattered exit the substrate at large radial distances away from the point beam origin. At 1 and 2 keV energies, the backscattered radial distribution is restricted to within about 40 and 80 nm from the point source beam origin, respectively. For higher energies of 15 and 20 keV, the backscattered radial spread increases drastically to about 2.1 and 3.6 µm, respectively. With increasing incident electron energy, the primary electron is capable of penetrating deeper into the substrate while also radially spreading within the substrate. Thus, inherently those electrons that suffer large angle scattering events at large radial distances away from the point source origin exit the substrate far away from the point source origin resulting in the broadening distributions. This observed broadening trend is also related to the penetration depth of the primary electrons. The ratio of the average penetration depth and the width of the radial backscatter spread slightly increases nonlinearly with increasing incident electron energy. As the energy is increased from 1 to 4 keV the ratio increases from 2.25 to 4.11. For 15 and 20 keV incident electron energies, the ratio is 10.58 and 13.61, respectively. Ideally, the ratio of the penetration
depth and the width of the backscatter electron spread should be minimized in order to constrain the backscattered electrons to exiting locations near the point source electron beam. It can be observed that the ratio increases at a slow rate with increasing incident electron energy.

Figure 6-3: Normalized backscattered radial electron distributions between 1 and 6 keV incident electron energies from a 2 nm thick monolayer on top of an infinitely thick silicon substrate.
Figure 6-4: Normalized backscattered radial electron distributions between 8 and 20 keV incident electron energies from a 2 nm thick monolayer on top of an infinitely thick silicon substrate.

In order to further investigate the relationship between the radial backscattering spread and penetration depth, backscattered depth distributions were also monitored for the various energies. As the electron traverses deeper into the substrate, the point electron beam spreads radially and these electrons suffering a large angle scattering event far away from the monolayer/substrate interface are eventually backscattered to larger radial distances away from the point source origin. The depth locations at which the incident electrons are backscattered were monitored with bin sizes of 1 nm and normalized by the total number of backscattered electrons for each incident electron.
energy. These normalized backscattered depth distributions are plotted for the various incident electron energies in Figure 6-5 and Figure 6-6. At 1 and 2 keV energies, the incident electrons traveled to a maximum depth of about 19 and 41 nm, respectively, before undergoing a large angle scattering event. For higher energies of 15 and 20 keV, the depth backscattered spread increased to about 1.1 and 1.8 µm, respectively. Therefore, as the primary electrons penetrate deeper into the substrate, the backscattering events are bound to occur at larger radial distances away from the point source origin whereby the backscattered electron also exits the substrate at larger radial distances. Also, for all incident electron energies the backscattered radial spread was found to be larger than the backscattered depth spread because each backscattered electron spreads radially before and after the large angle scattering event whereby traversing more radially within the film stack. It should also be observed that the backscattered depth spread is much smaller than the average penetration depth observed for each incident electron energy since backscattered electrons at large penetration depths do not retain sufficient energy to reach the monolayer/silicon interface. The ratio of the backscattered depth spread to the average penetration depth is approximately in the range of 3-4 for the various incident electron energies. Thus, increasing incident electron energies results in larger depth backscatter spreads where the primary electron spreads more radially which in turn increases the backscattered radial spread.
Figure 6-5: Normalized depth distributions for backscatter electrons between 1 to 6 keV incident electron energies from a 2 nm thick monolayer on top of an infinitely thick silicon substrate.

Figure 6-6: Normalized depth distributions for backscattered electrons between 8 to 20 keV incident electron energies from a 2 nm thick monolayer on top of an infinitely thick silicon substrate.
Further, backscattered electrons were classified into different types according to the number of large angle scattering events suffered before reaching the monolayer/silicon interface. Typically a backscattered electron suffers a single large angle scattering event before exiting a medium. After undergoing a large angle scattering event the electron can suffer another large angle scattering event and remain absorbed within the substrate. Sometimes the electron could again suffer a large angle scattering event and possibly escape the substrate. These backscattering processes can repeat themselves resulting in backscattered electrons that have undergone an odd number of large angle scattering events in order to reach the monolayer/silicon interface. Here, a backscattered electron suffering a single large angle scattering event will be referred to as a Type 1-scattering event. Similarly, a Type 3-scattering event refers to a backscattered electron which has suffered three large angle scattering events. A similar definition is adopted for a Type 5, Type 7, or Type 9-scattering events. Figure 6-7 plots the fractions of the type of scattering events at various incident electron energies. For most energies, about half of the backscattered electrons are of Type 1-scattering event. As expected, the fraction of the type of scattering event increases from a Type – 9 to a Type – 1 scattering event. That is, a backscattered electron has an increasing probability of suffering 1, 3, 5, 7, and 9 large angle scattering events. It can also be observed that the fraction of a Type – 1 scattering event increases from about 0.41 to 0.65 as the incident electron energy is decreased from 20 to 1 keV. Similarly, a Type – 3 scattering event also slightly increases with decreasing incident electron energy from 20 to 1 keV. The other types of scattering events decrease drastically and tend to zero with decreasing incident electron energies. Thus at low incident electron energies, the backscattered electron are primarily those
which undergone a Type – 1 or a Type – 3 scattering event. At moderate and high incident electron energies, the incident electrons have a higher probability of suffering numerous large angle scattering events.

Figure 6-7: A plot of the type of scattering event suffered by backscattered electrons for various incident electron energies that range from 1 to 9 large angle scattering events before escaping the substrate.
6.3.3. *Energy distribution*

The energy absorbed by the monolayer is contributed through forward scattered electrons prior to entering the substrate and backward scattered electrons exiting from the substrate. In order to monitor the energy deposition, the monolayer film was discretized into annuli of 1 nm radius with 2 nm thicknesses and the collision cells were incremented with the energy that was lost by incident electron prior to its previous scattering event. Figure 6-8 plots the total forward and backward scattered energy deposited in the monolayer per incident electron. As expected, the energy deposited in the monolayer increases as the incident electron energy is decreased as incident electrons have a higher probability of interacting with the monolayer prior to entering the substrate. The backscattered energy deposition is higher than the forward scattered energy deposition for almost all incident electron energies. The ratio of the backward to forward scattered energy deposition is about 3 for all energies studied. The ratio of total energy deposited in the monolayer at 1 and 2 keV is about 3. The ratio is about 3 and 2 as the energy is increased from 2 to 4 and from 4 to 6 keV, respectively. The energy deposition decreases with increasing incident electron energy as a consequence of decreasing interactions between the incident electrons and the monolayer. It was previously observed that the collisions per incident electron decreased exponentially with increasing incident electron energies. A similar decreasing exponential trend in total energy accumulation in the monolayer with increasing incident electron energy is observed.
The energy distribution per incident electron is plotted for 1, 2, and 4 keV incident electron energies in Figure 6-9. The profiles tend to exhibit the summation of a narrow and a broad Gaussian distribution corresponding to the forward and backward scattered energy distribution, respectively. The forward scattering energy contribution is minimized to a narrow width of about 2 nm or less for the incident electron energies since the electrons are radially constrained in the monolayer film. However, the backscattered electrons are distributed far away from the point origin and result in a broad Gaussian energy distribution similar to that of the radial backscattered distribution. At 1 keV incident electron energy, the distribution extends to about 50 nm away from the point source origin. The backscattered energy distribution becomes broader with increasing incident electron energy due to a broadening radial backscattered electron distribution.
However, the energy deposited by these backscattered electrons at higher energies decreased due to a smaller collision probability with the monolayer. Therefore, a tradeoff exists between throughput and resolution attainable with the monolayer imaging systems. At low energies, energy deposited in the monolayer can be maximized but a broad backscattered energy distribution restricts resolution. Alternatively, high incident electron energies can be utilized to reduce the broad backscattered energy distribution in order to obtain higher resolution but drastically reduces throughput since collision probability is lowered.

![Energy distribution](image)

**Figure 6-9:** Energy distribution in the 2 nm thick monolayer film per incident electron for 1, 2, and 4 keV incident electron energies.
6.4. Summary and Conclusions

In this chapter we have explored the benefits and limitations of an ultrathin electron beam imaging approach using self assembled monolayers. Due to the use of an ultrathin film, the forward scattering spread was contained to within 2 nm of the point source origin for an incident electron energy as low as 1 keV. At energies below 10 keV, the resolution of this ultrathin film imaging approach was restricted by backscattered electrons from the substrate. However, the major advantage of using low energies is that direct collisional interactions were found to increase in an exponential manner for energies below 10 keV whereby the dose required to pattern these monolayers could be dramatically reduced. With increasing incident electron energy the radial and depth backscatter spreads increased proportionally as the incident electrons were capable of penetrating to larger depths into the substrate. Concurrently, the incident electrons also spread radially and those electrons which suffer a large angle scattering event eventually exit the substrate at larger radial distances from the point source origin. However, backscattered electrons exiting the substrate with energies above 10 keV interact minimally with the monolayer and deposited a negligible amount of energy to the monolayer. Hence, the use of high incident electron energies was found to enhance the resolution attainable using this ultrathin imaging approach. However, a major disadvantage of using high incident electron energies is the high electron beam dose requirements necessary for transformation of the monolayer.

In utilizing this ultrathin film imaging approach, low incident electron energies would be preferred such that a high throughput process could be developed. Thus,
optimization of the process at low incident electron energies requires the minimization of backscattered electrons from the substrate. A possible approach would be to use a spacer layer between the monolayer and the substrate which is transmissive to the incident electrons. This approach takes advantage of the observation that the incident electrons that have traversed to large depth distances away from the monolayer have a lesser probability of being backscattered. Even those electrons that are backscattered would not retain sufficient energy to traverse back to the monolayer. Also, another variation of this approach is the use of a thiol based monolayer deposited on top of a gold substrate. Due to the higher atomic number of the gold a larger backscattering coefficient as compared to silicon would be expected. However, the penetration depth of incident electrons will be much lower due to the higher density of gold which could result in a smaller radial backscattering spread as compared to a silicon substrate. The consequences of these various approaches require further Monte Carlo studies for optimization and process refinement of this unique ultrathin film monolayer electron beam imaging method.
CHAPTER 7

7. Summary and Recommendations for Future Work

7.1. Summary

In this thesis, advances have been made in developing and enhancing the performance of inorganic resist materials for high resolution electron beam lithography. A novel inorganic resist approach utilizing metal-organic precursors was developed and characterized for application in direct write electron beam patterning of metal oxide structures. Sub-100nm patterning was demonstrated using this approach with single, dual, and multicomponent precursor systems. Further, the electron beam imaging performance of the most widely used inorganic resist material to date, hydrogen silsesquioxane was enhanced through the addition of sensitizers such as photodecomposable bases and photobase generators. The influence of high atomic number species in an electron beam resist was studied through Monte Carlo simulations. An incident electron energy regime was established where inorganic resist behavior was found to be better than organic resists. The influence of nanoparticles in an electron beam resist and the electron beam patterning of self assembled monolayers were also investigated.

A novel metal-organic imaging scheme was developed using single, dual, and multicomponent precursor systems. Precursor systems based on titanium, strontium, and
barium metal centers with varying chelating and nonchelating ligands were investigated. Carboxlyate based titanium precursors demonstrated better hydrolytic stability than alkoxide based systems and the addition of barium and strontium precursors to the carboxylate based titanium precursor also provided a stable patterning film. Also, the unstable titanium alkoxide precursor was found to be stabilized through the addition of stable barium and strontium precursors to the patterning matrix. High resolution was exhibited by all precursor systems but the inclusion of high atomic number species precursors in the patterning matrix drastically enhanced its imaging performance. It was postulated that the addition of high atomic number species to the patterning matrix produced a higher yield of secondary electrons within the film that reduced patterning dosage. The sensitivity of the precursor matrix was found to be inversely proportional to the effective atomic number of the patterning film. The titanium precursor by itself exhibited a sensitivity of only about 495 $\mu$C/cm$^2$. The addition of a barium precursor to the patterning matrix in a 1:1 molar ratio along with the titanium precursor enhanced the sensitivity to 157 $\mu$C/cm$^2$. Further, the addition of a strontium precursor in a 1:1:1 molar mixture containing the barium and titanium precursors enhanced the sensitivity to about 70 $\mu$C/cm$^2$. The addition of the high atomic number species also enhanced the etching performance in ashing and oxide plasmas. The etch resistance of the precursor films was found to strongly depend upon the extent of conversion to its respective metal oxide form. In an oxygen ashing plasma, an as coated precursor lost most of its original thickness until a metal oxide capping layer was formed that inhibited further etching. However, thermally converted precursor films demonstrated high etch selectivities greater than 100:1 as compared to hard baked novolac. In an oxide etching plasma, the
thermally converted precursor films exhibited slightly greater etch resistance than silicon dioxide. The etch selectivity was about 1.5:1. The enhancement in etch performance through the addition of high atomic number species such as barium and strontium to the patterning matrix is due to the difficulty in formation and low volatility of etch products. The single, dual, and multicomponent precursor systems demonstrated high resolution patterning capabilities for direct patterning of metal oxide structures. The titanium carboxylate precursor demonstrated 70 nm isolated patterning at 25 keV incident electron energy with a film thickness of 180 nm. The multicomponent barium: strontium: titanium precursor demonstrated 100 nm patterning with a film thickness of about 300 nm at 10 keV incident electron energy.

The electron beam sensitivity of hydrogen silsesquioxane (HSQ) was enhanced by including sensitizers that decompose to generate nucleophiles which catalyze the conversion of the silicon hydride (Si-H) moieties in HSQ into the insoluble siloxane (Si-O-Si) network. In this work, the consequences of including triphenylsulfonium hydroxide (TPS-OH) and 2-nitrobenzyl N-cyclohexylcarbamate (NBC) as a photodecomposable base (PDB) and photobase generator (PBG) were investigated, respectively. The sensitizers can aid in hydrolysis of the Si-H to the Si-OH functionalities and in the further condensation of silanol groups. It is well known that the hydrolysis state of the HSQ solution changes during the storage time as Si-H functionalities are prone to hydrolysis that result in the formation Si-OH groups. Thus, the hydrolytic state of the solution can affect the performance of the sensitizers depending upon whether catalyzation of the hydrolysis or condensation reaction is preferred. It was found that inclusion of sensitizer mainly aided in enhancing the
performance of aged HSQ solutions. Therefore, the condensation of the Si-OH functionalities was aided through the addition of the sensitizers. It was found that using 5 wt% loadings of TPS-OH or NBC in HSQ in conjunction with a post-exposure bake process enhanced the sensitivity of large features exposed at 25 keV accelerating voltage by approximately 50 and 40 %, respectively. Similarly, the electron beam doses required to print single pixel wide lines exposed at an accelerating voltage of 25 keV were enhanced by 70 and 50%, for 5 wt% loaded TPS-OH or NBC films, respectively. It was also found that the basicity and nucleophilic strength of the sensitizer affects the rate of the undesired hydrolysis reaction of HSQ which occurs in solution. For the sensitizers used in this study, the sterically hindered TPS-OH is a poor nucleophile which stabilized the solution against condensation and formation of a siloxane network, while the moderately nucleophilic NBC slightly decreased the stability of the solution. The stabilization of the solution through addition of TPS-OH was postulated to occur through the capping of silicon-hydroxyl groups by the triphenylsulfonium cation. Also, it was found that thermal baking alone could be utilized to enhance the sensitivity of HSQ, but a loss in contrast was observed with pre and post patterning thermal treatments. The combination of either TPS-OH or NBC and a post-exposure bake produced superior results, as compared to thermal baking alone, in terms of increasing the sensitivity of aged HSQ while maintaining moderate contrast.

The consequences of high atomic number species and nanoparticles in an electron beam resist was investigated through Monte Carlo simulations. A model study was performed by tagging a silicon or titanium atom onto a polymer in order to study the effects of high atomic number species on electron scattering. With the inclusion of high
atomic number species, the ratio of elastic to inelastic collisions per incident electron increased along with the average elastic scattering angle while the average inelastic scattering angle stayed approximately constant. The point electron spread in the high atomic number species containing films was found to be smaller as compared to an organic film at high incident electron energies of 75 and 100 keV where the incident electrons are radially constrained due to the increased density with addition of high atomic number species. The consequences of nanoparticle addition to an electron beam resist used to primarily enhance etch properties was also studied. The effective film properties were assumed to follow a simple linear mixing rule of the polymer and nanoparticle properties. In order to verify the assumption, a percolative study was performed through random assignment of a lattice as consisting of a nanoparticle or a polymer. A threshold grid length was determined for various nanoparticle loadings in the lattice beyond which the effective density approximation was valid. A minimum of 4-5 nm was required to satisfy the calculation of effective film properties from the simple linear mixing rule. The simulations were focused on a silica (SiO₂) loaded polymethylmethacrylate (PMMA) film at different nanoparticle loadings and incident electron energies. It was found that the point electron spreads for nanoparticle loadings ranging from 2 to 10 wt% were comparable to a film without nanoparticles for high incident electron energies of 75 and 100 keV due to the increased radial containment resulting from the increase in density with higher nanoparticle loadings.

The electron beam patterning of a self assembled monolayer was also investigated through Monte Carlo simulations. An ideal model of a 2 nm thick polymethylmethacrylate (PMMA) film on top of a silicon substrate was used to monitor
the trajectories of forward and backward scattered electrons for incident electron energies ranging from 1 to 20 keV. It was found that the average number of collisions between incident electrons and the monolayer tended towards zero for energies greater than 10 keV. As the incident electron energy increased, the forward and backscattered electron spreads decreased and increased, respectively. The forward scattering electron spread was contained to within 2 nm in the monolayer even at 1 keV energy. At 1 and 2 keV energies, the backscattered radial electron spread were 40 and 80 nm, respectively. The backscattered radial spreads increased to 2.1 and 3.6 µm for 15 and 20 keV incident electron energies, respectively. The broadening of the backscattering radial distribution was found to depend on the depth distribution of backscattered electrons which also increased with incident electron energy. As the incident electron energy was increased from 1 to 20 keV, the depth backscatter spread increased from 19 nm to 1.8 µm. With increasing incident electron energy the point electron beam penetrates deeper into the substrate while also concurrently spreading radially and as a consequence those electrons which are backscattered at large depth distances eventually exit the monolayer/substrate at larger radial distances away from the point source origin. The deposited energy was found to be a summation of a narrow and broad Gaussian distributions representing the contribution from forward and backward scattered electrons, respectively. The broad backscattered energy distribution was found to decrease in intensity with increasing incident electron energy due to a decreasing collisional probability. It was found that the broad backscattered electron energy distribution was negligible for incident electron energies greater than about 6 keV. However, at these high incident electron energies, the
interaction probability between the incident electrons and the monolayer is decreased thereby drastically affecting the throughput achievable with this unique process.

7.2. Recommendations for future work

The metal-organic electron beam imaging scheme developed in this thesis has demonstrated excellent resolution but requires high electron beam dosage for defining patterns. The imaging doses can be reduced using a dual process with a pre-patterning partial conversion step through thermal baking or photolysis but results in reduced process contrast. The partial conversion can also be achieved through a mixture of a stable and unstable precursors in a patterning matrix. The unstable matrix is prone to self conversion through hydrolysis that would provide partial conversion of the reaction matrix whereby reducing the electron beam patterning doses. A host of unstable alkoxide based titanium precursors can be utilized for such a study along with the stable carboxylate titanium precursor. Different molar ratios of the alkoxide and carboxylate based titanium precursors can be studied to determine the effects of including an “auto-catalytic” self converting precursor material. There would be a limitation to the extent of addition of the unstable alkoxide precursor that would result in blanket conversion and prevent patterning to be achieved. Therefore, relatively small molar ratios of 1:5, 1:4, 1:3, 1:2, and 1:1 of the alkoxide:carboxylate should be studied. The exposure delay time is also critical as the host matrix is expected to convert by itself and patterns cannot be delineated whence a critical conversion limit has been exceeded from too long of an exposure delay.
The use of ultra-high atomic species precursors can also be studied to enhance the electron beam imaging performance of the metal-organic imaging scheme. It was shown that the sensitivity of the precursor film was inversely proportional to the effective atomic number of the patterning matrix. The best sensitivity achieved with the metal-organic imaging approach was about 70 µC/cm² using a 1:1:1 barium:strontium:titanium multicomponent precursor. The barium and strontium precursors have atomic numbers of 56 and 38, respectively. It would be possible to utilize other commonly available ultra-high precursors based on lead, bismuth, or zirconium, that have atomic numbers of 82, 83, and 40, respectively. Based on the trend observed upon incorporation of barium and strontium precursor to the titanium precursor, the effects of including such ultra-high atomic number precursors could enhance the sensitivity by two-fold. The effective atomic number of a lead:zirconium:titanium precursor system is 187 as compared 116 for a barium:strontium:titanium system. Thus, the incorporation of the ultra-high atomic number precursors can possibly enhance the sensitivity to about 35 µC/cm².

In this thesis, it was shown that the imaging performance of hydrogen silsesquioxane could be enhanced through the addition of sensitizers. However, the effects of the sensitizers were mainly in enhancing the condensation reaction of the silanol functionalities that are formed as the solution ages due to the hydrolytic susceptibility of the silicon hydride functionality. An alternative resist material that could also be investigated is methylsilsesquioxane (MSQ) that contains methyl groups at the corners of the silicon cages that are much less prone towards hydrolysis as compared to the hydrogen end groups. With HSQ, the imaging reaction is assumed to proceed through the conversion of the hydrolyzed hydride functionalities to the form the silanols
that eventually condense to transform the caged species to the linear network. However, this type of imaging reaction is not conceivable in MSQ since the methyl group is not readily hydrolyzed. Therefore, the imaging reaction should be entirely through electron beam degradation of the caged silisquioxane molecule. That is, electron beam irradiation should cause cleavage of the Si-O or Si-CH₃ groups in order to breakdown the caged species and form a insoluble network. Even though a higher electron beam dose might be required to pattern the MSQ material, it would eliminate the hydrolytic instability that affects the performance of the HSQ resist during storage time.

The Monte Carlo studies on the effects of high atomic number species were primarily performed for high incident electron energies where radial constraint afforded by the high density inorganic resist can be taken advantage. Alternatively, low incident electron energies could also be utilized to radial constrain the electron beam. The interaction of high atomic number atoms with low incident electron energies requires the utilization of Mott elastic scattering cross section and the tracking of secondary electron trajectories beyond the 1ˢᵗ knock off electron that was performed during the simulations in this thesis. A very high secondary electron yield would be expected at low incident electron energies due to the high inelastic collision probability along with large electronic shells afforded by the high atomic number atoms. Therefore, secondary, tertiary, quaternary, and other electrons would be expected to be generated during the electron beam interaction process. The cascade generation of electrons could also aid in drastically reducing the dose required to pattern these materials. With these simulations, a low energy regime could possibly be established where comparable resolution to an organic resist could also be achieved. Therefore, utilization of inorganic resists might
also be desired at low incident electron energies along with the high incident electron energies that were determined in the Monte Carlo simulations performed in this thesis.

The Monte Carlo study performed on the electron beam patterning of self-assembled monolayers was performed for film growth on a silicon substrate. Another common method of self assembly is through the growth of thiol based monolayers on a gold substrate. Even though the thickness of the monolayer should be comparable, the gold substrate behaves drastically different as compared to a silicon substrate. Its density (19.33 g/cm\(^3\)) is about then fold as compared to silicon (2.33 g/cm\(^3\)) and its atomic number (89) is greater than six fold as compared to silicon (14). The differences in the substrates will drastically affect the interaction with impinging electrons. The backscattering coefficient of gold is much higher than silicon. At 20 keV incident electron energy, the backscattering coefficient of gold and silicon are 0.15 and 0.40, respectively, as calculated from the Everhard empirical relationship. The backscattered electron distribution would be expected to be much smaller due to the high density of gold which restricts radial spreading within the substrate. However, the effects of secondary electrons generated at the near the monolayer / gold interface can have a greater impact on the imaging performance. The higher atomic number gold substrate will provide a higher secondary electron yield. It would be possible to reduce the radial backscattered spread that affects the resolution attainable at low incident electron energies by using gold as the substrate. Hence, high throughput as well as high resolution can be maintained with the self assembled monolayer process.
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Augustin Jeyakumar was born on April 1st, 1978, in Madurai, India to Ayyamperumal Jeyaprakash and Margret Stella Packiam. He emigrated to the United States of America in the early 1990’s and finished his high school studies in Gainesville, Florida, in 1995. He attended the University of Florida wherein obtaining a Bachelor of Science in Chemical Engineering with high honors in 1999. He performed research under the guidance of Dr. Mark Orazem and finished his undergraduate thesis entitled “Impedance spectroscopy characterization of cement”. He began pursing the Doctor of Philosophy in the School of Chemical & Biomolecular Engineering at the Georgia Institute of Technology in the fall of 1999. His doctoral thesis research has been focused on the development of inorganic resist systems for electron beam lithography and understanding their behavior using Monte Carlo simulations. He has been guided in his thesis research by Dr. Clifford L. Henderson.